The measurement of Total Oxygen in filled BIB wine

"There shall be one measure of wine throughout our whole realm"

The Magna Carta, 1215

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Wine BIB O_2 measurements / Summary

Part 1: Wine BIB shelf life, by Patrick Shea, Vitop

- 1.1) Goal
- 1.2) Key Parameters
- 1.3) The headspace problem

Annex: O_2 measurement definitions

Part 2: Measurement technologies, by Jean-Claude Vidal, INRA

- 2.1) Main measurement technologies
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Photo credits of oxygen sensor instruments and measurements: Marc Maupas, Patrick Shea, Sophie Vialis

Part 1: Wine BIB shelf life, by Patrick Shea, Vitop

1.1) Goal

1.2) Key Parameters

- Wine
- SO_2
- Filtration and sterility
- Oxygen pickup during filling
- Package permeability
- Damage to barrier film
- Storage temperatures

1.3) The headspace problem

Annex: O_2 measurement definitions

Definition of Wine BIB Shelf Life

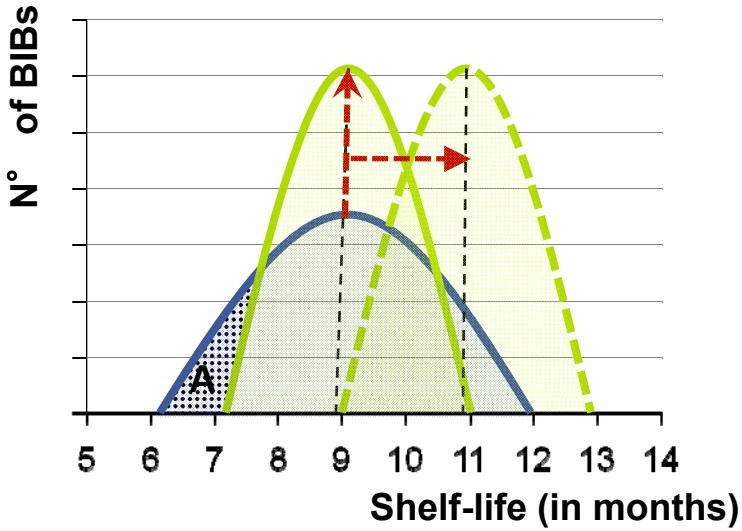
Length of time before the wine is considered unsuitable for consumption

This is the **interval between the filling of the BIB and the last glass consumed**

Goal for retailers and fillers: reach or exceed a target (ex: average of 9 months) while minimizing variance

SHELF LIFE GOAL:

Bell curves **tightened** (less variance) and/or **shifted** to the right



When is BIB wine unacceptable?

- **How long can a BIB wine hold up?**
  - ➡ **This depends upon:**
    - **Changes** that occur in the wine (taste, color, etc.)
    - A **judgment** that these changes are unacceptable

The judgment of a BIB wine will be more severe if:

→several **conditions** must be met to "pass" the test
(for example: free SO_2 > 10 mg/l *and* taste *and* color acceptable)

→**professional tasters** are used rather than typical consumers

→**compared** to the same wine in glass bottle with a screw-cap

Even when all key shelf-life parameters are mastered:

→a BIB wine may be judged to not last over **9 months** if evaluated under severe conditions

→the same wine might be considered acceptable for most wine consumers for up to **12 months**

A special note to importers and retailers

Wine importers and retailers should:

- **Fix realistic shelf life requirements** (for example 9 months max.) that are adjusted to the particular wine.

- **Adopt good practices** (low storage and transport temperatures and quick rotation)

- **Be more concerned about helping suppliers meet overall shelf-life goals rather than fixing performance criteria based upon selected parameters, particularly if measurement issues are highly complex and non-standardized.** Examples of criteria not to include in specifications: requiring that Dissolved Oxygen (DO) pickup be < 0.5 mg/L or that the permeability of the bag should be < 0.5 $cm^3/m^2/day$.

- Refer to the Good of Practices for the filling of wine in BIB

Guide de Bonnes Pratiques
pour le conditionnement du vin en BIB
Guide for Good Practices
for the filling of wine in BIB
BIB
BIB

Seven Ways to Extend Wine BIB Shelf-Life

It is possible to push forward the limits of shelf life by:

1) Selecting **certain types of wines**

2) Adding appropriate amounts of **SO_2**

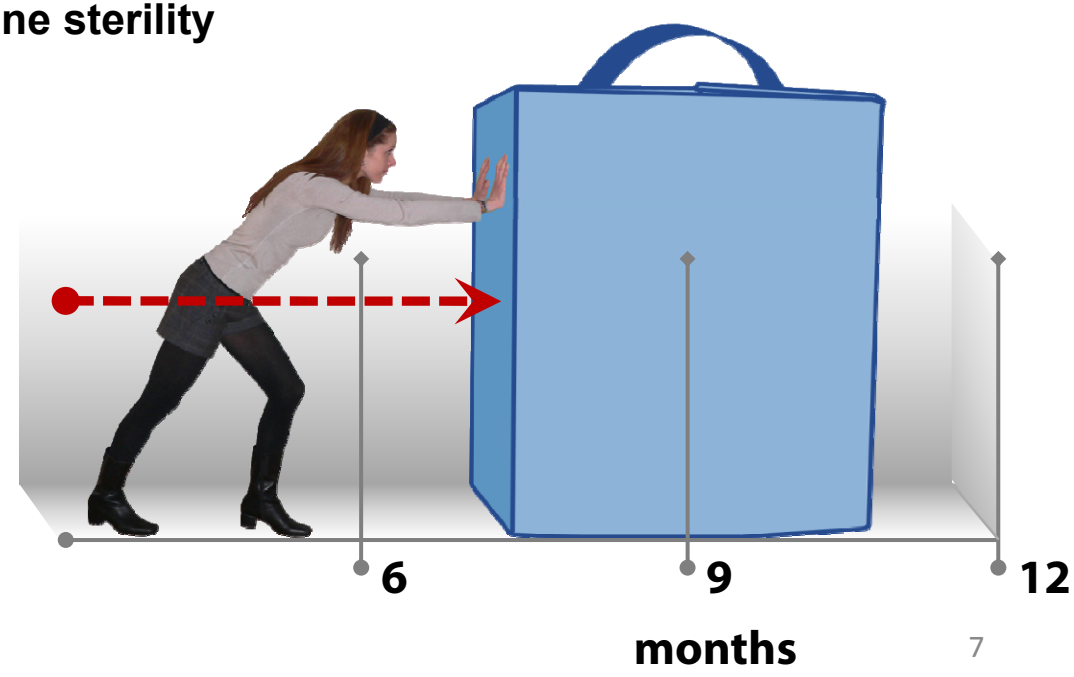
3) Proper **final filtration** and **filling line sterility**

4) Minimizing **oxygen pickup** by the filling process

5) Selecting a **package** with low gas permeability

6) Minimizing **damage** to the barrier film

7) Minimizing storage **temperatures**



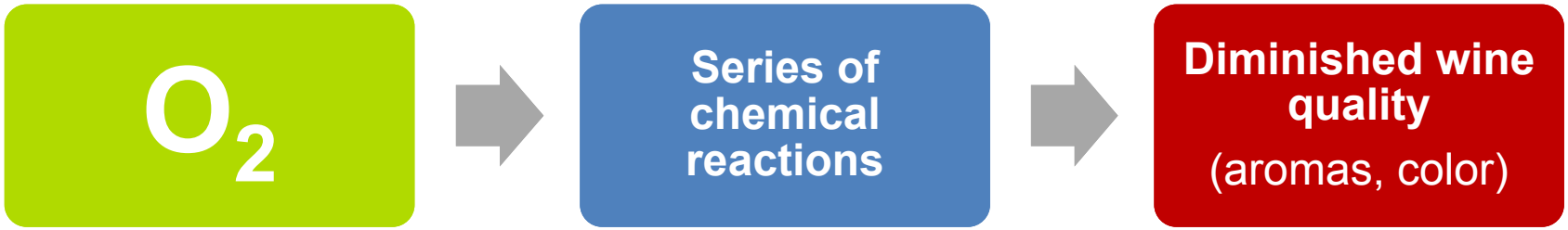
Shelf-Life Factor 1: The Wine

Expected shelf-life depends upon the **specific wine chosen**

On the average BIB wines will **have a longer shelf life** if they:

- →are **red** rather than white because reds have more anti-oxidative polyphenols
- →have **high alcohol** and **high acid** (low pH)
- →have a **low level of initial dissolved oxygen** before bottling
- →have **not already suffered many oxidative reactions**

A wine that is oxidized is permanently damaged!



Shelf-Life Factor 2: SO_2

- **SO_2 added to wine** will contribute to **extended shelf-life**

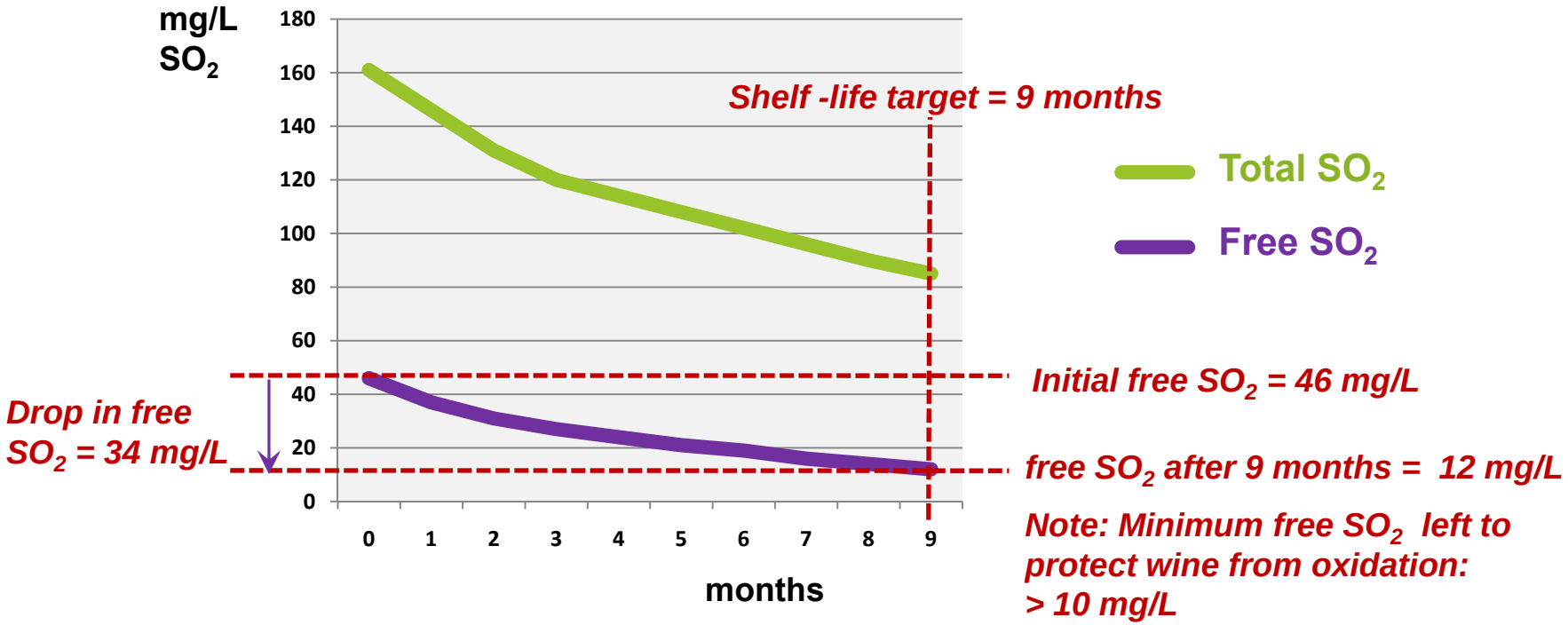
- The level of **free SO_2 upon filling** is often **25 to 50 mg/l** → this will fall over time

- The ideal amount must be **determined by the winemaker** and will depend upon:

    - "burnt match" odor risk
    - Cumulative oxygen (measured or expected)
    - shelf life target
    - pH of the wine
    - microbiological risks
    - other factors

Shelf-Life Factor 2: SO_2

Example of the fall of Total and Free SO_2 for a French Chardonnay in BIB at 20 ℃

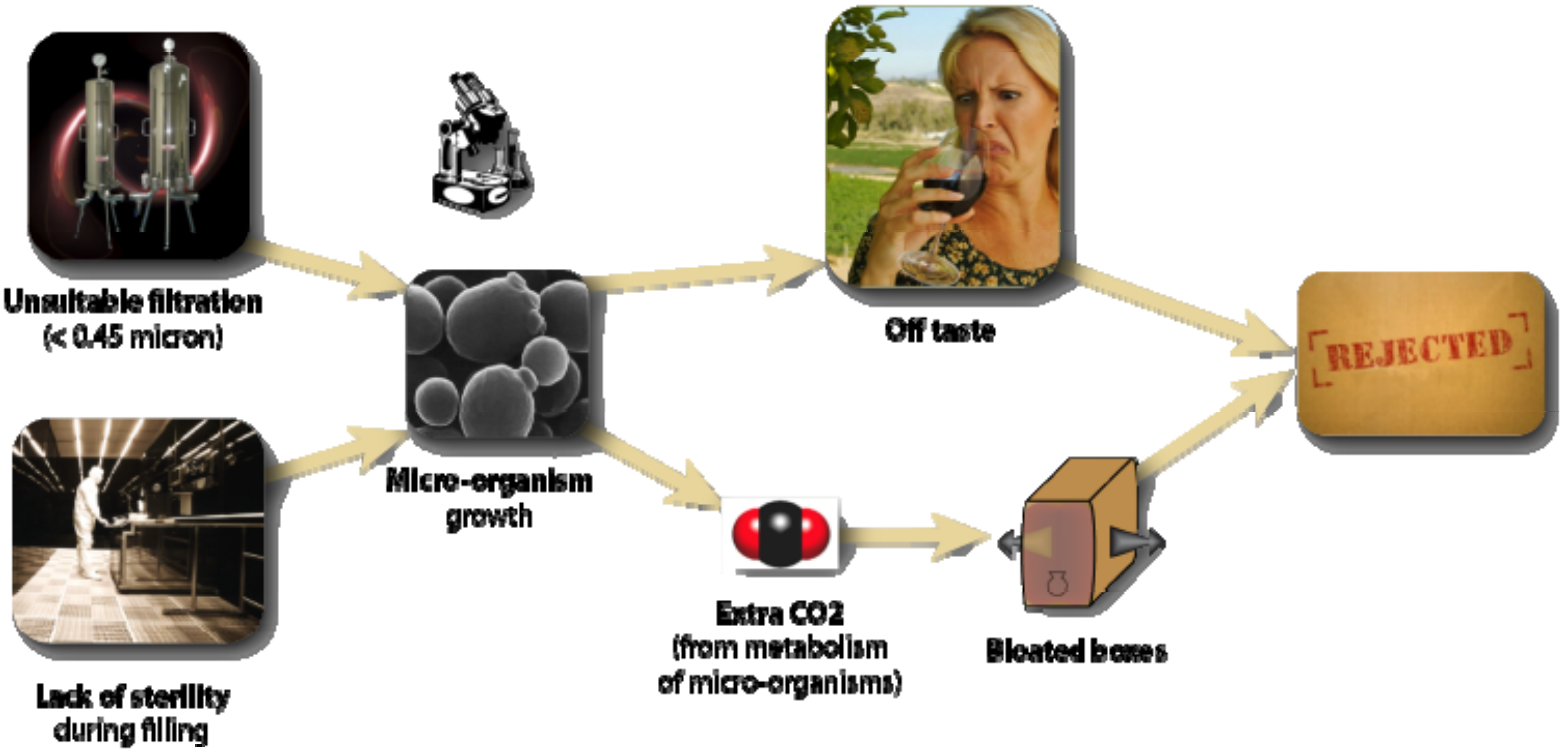


Source: INRA 2004, Study for Performance BIB

Shelf-Life Factor 3: Microbiological Control

Wine BIB shelf-life can be greatly decreased by **inadequate final filtration** or **lack of sterility** during the filling operation

Periodical microbiological analysis + sound hygiene practices can greatly reduce the risk



Shelf-Life Factor 4: O_2 Pickup During Filling

Important to minimize since **1 extra mg/l of O_2 reduces shelf life by one month (INRA 2004)!**

Oxygen pickup during filling **= Δ dissolved O_2** in the wine + **Air cone O_2**

Air cone O_2 is the result of both the **volume** of the air cone and the **% of oxygen** inside

- **Key factors to control:**
  - → filling valve technology
  - → vacuum pack to remove air
  - → amount of initial O_2 in the empty package
  - → filling table adjustments
  - → nitrogen flushing of tap and gland to reduce O_2

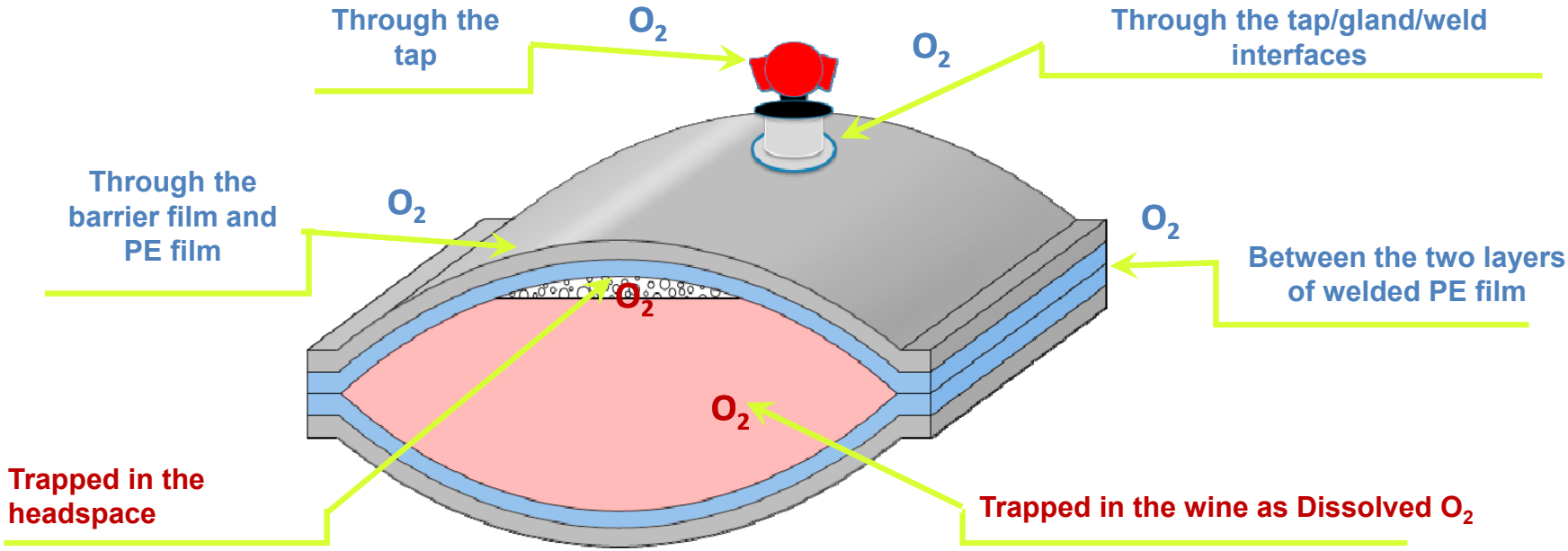
Shelf-Life Factor 5: O_2 Permeation of Package

Total Life Cycle Package Oxygen (see schema page 22)

= **O_2 pickup during filling** (DO pickup + headspace O_2)

+ **Filled Package O_2 ingress during several months after filling**

⇨ **Quantify the sources of O_2 and pinpoint potential improvement areas**



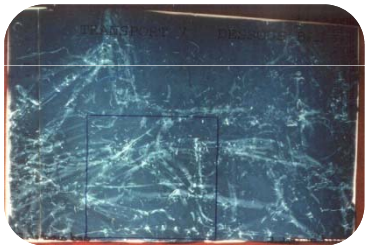
Shelf-Life Factor 6: Damage to Package

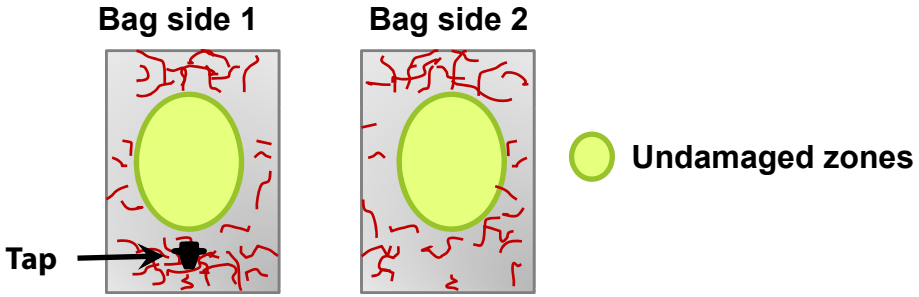
Damage to the BIB package, particularly to the barrier film, will shorten shelf-life

BIB bags can be examined periodically after filling and after they have gone through the distribution channels

Flex-cracking is normal but if zones of **excessive damage** are identified, causes should be determined and corrective action taken

Metalized polyester BIB bag examined with back-light
by Gilles Doyon, Agriculture Canada





- It is also important **to check the residual space left in the box** (normally + 0.5 litres for a 3 litre box) since this can also have an impact on the jiggling of the filled bag and resulting stress on the film

Shelf-Life Factor 7: Temperature

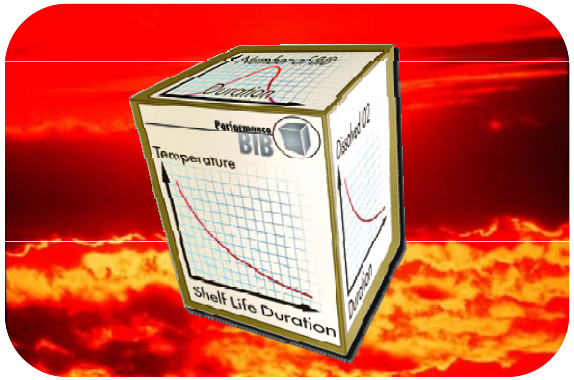
High storage temperatures are the mortal enemy of BIB wines!

Research by the INRA in France has shown that an **increase in storage temperature by 10** ℃ (from 20 ℃ to 30 ℃) will reduce wine BIB **shelf-life by half!**

→*This is due to both increased **oxygen transmission rates** of the package and to increased rates of **chemical reaction** in the wine*

→ *Storage and transport temperatures should be maintained under 25* ℃

Other research suggests that substantially heating up a filled met-pet BIB bag may permanently diminish the oxygen barrier of the film



Who can guarantee wine BIB shelf life?

Should the BIB bag manufacturer guarantee wine BIB shelf-life?

➡**No.** Because the bag supplier only controls one of the seven key parameters that determine shelf-life

Parameter	Who is responsible?
The wine	Winery
SO_2	Filler
Microbiological control	Filler
O_2 pickup during filling	Filler
Package O_2 ingress	Bag manufacturer
Package damage	Filler/Distributor
Temperature	Filler/Distributor

Should the BIB filler guarantee wine BIB shelf-life?

➡**Partially,** but even if the filler also supplies the wine and buys a quality bag, not all parameters are fully controllable , since damage to the package or high temperatures can also occur after the BIB wines leave the filling centre

A graphical representation of life cycle O_2 management

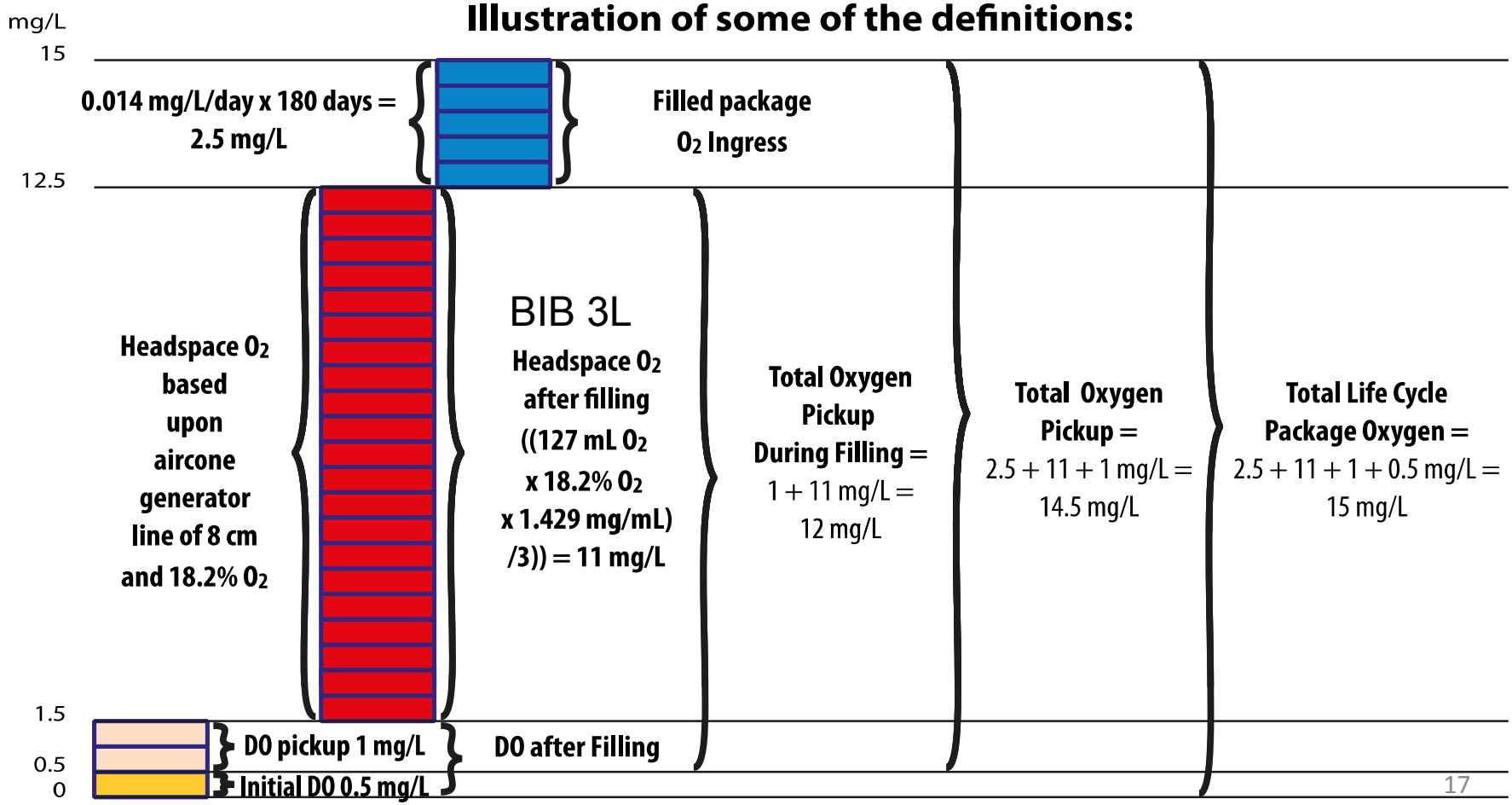
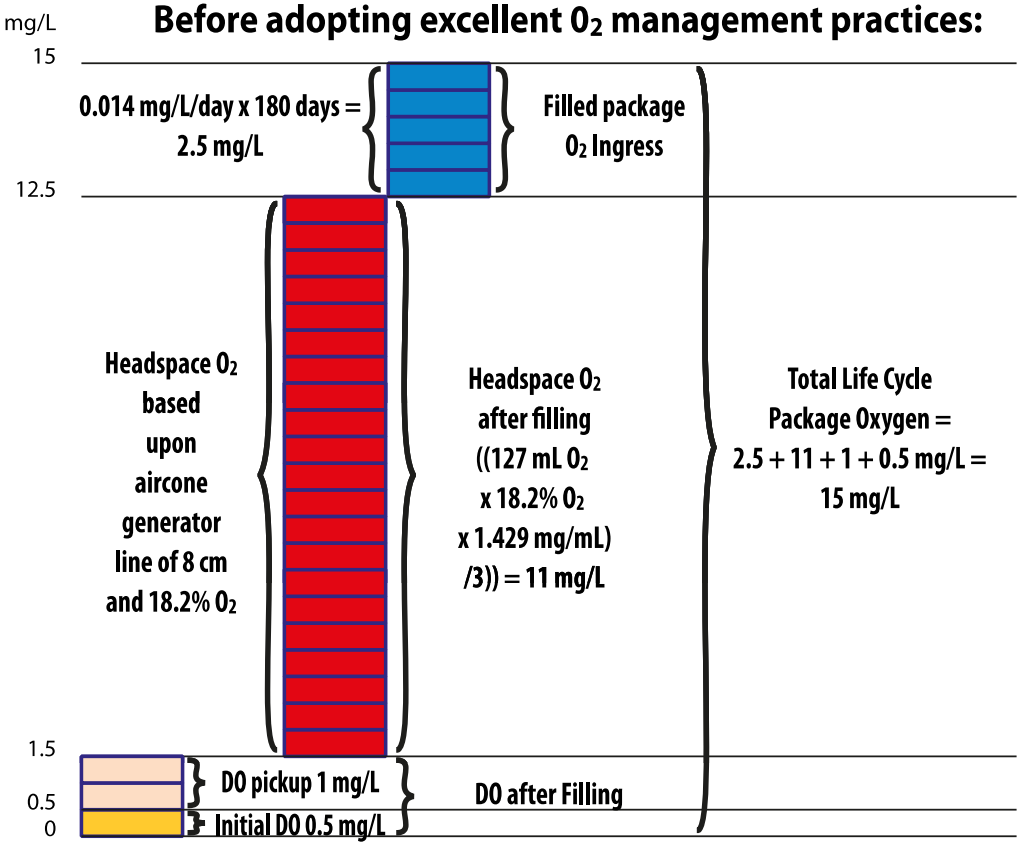


Illustration of some of the definitions:
mg/L
15
12.5
1.5
0.5
0
0.014 mg/L/day x 180 days = 2.5 mg/L
Filled package O2 Ingress
Headspace O2 based upon aircone generator line of 8 cm and 18.2% O2
BIB 3L
Headspace O2 after filling ((127 mL O2 x 18.2% O2 x 1.429 mg/mL) /3)) = 11 mg/L
Total Oxygen Pickup During Filling = 1 + 11 mg/L = 12 mg/L
Total Oxygen Pickup = 2.5 + 11 + 1 mg/L = 14.5 mg/L
Total Life Cycle Package Oxygen = 2.5 + 11 + 1 + 0.5 mg/L = 15 mg/L
DO pickup 1 mg/L
Initial DO 0.5 mg/L
DO after Filling

A graphical representation of life cycle O_2 management

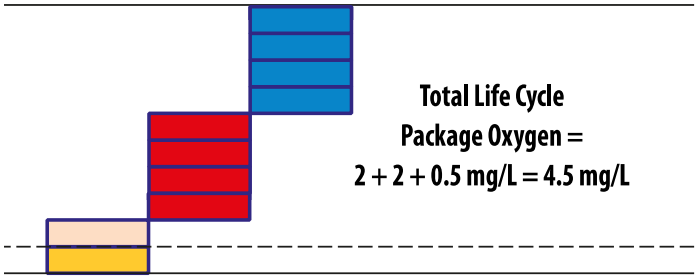

mg/L
15
12.5
1.5
0.5
0
Before adopting excellent O2 management practices:
0.014 mg/L/day x 180 days = 2.5 mg/L
Filled package O2 Ingress
Headspace O2 based upon aircone generator line of 8 cm and 18.2% O2
Headspace O2 after filling ((127 mL O2 x 18.2% O2 x 1.429 mg/mL) /3)) = 11 mg/L
Total Life Cycle Package Oxygen = 2.5 + 11 + 1 + 0.5 mg/L = 15 mg/L
DO pickup 1 mg/L
Initial DO 0.5 mg/L
DO after Filling

After adopting excellent O_2 management practices:

Reducing the aircone generator line from 8 cm to 5 cm (34 mL air) and O2 content from 18.2 % to 12%

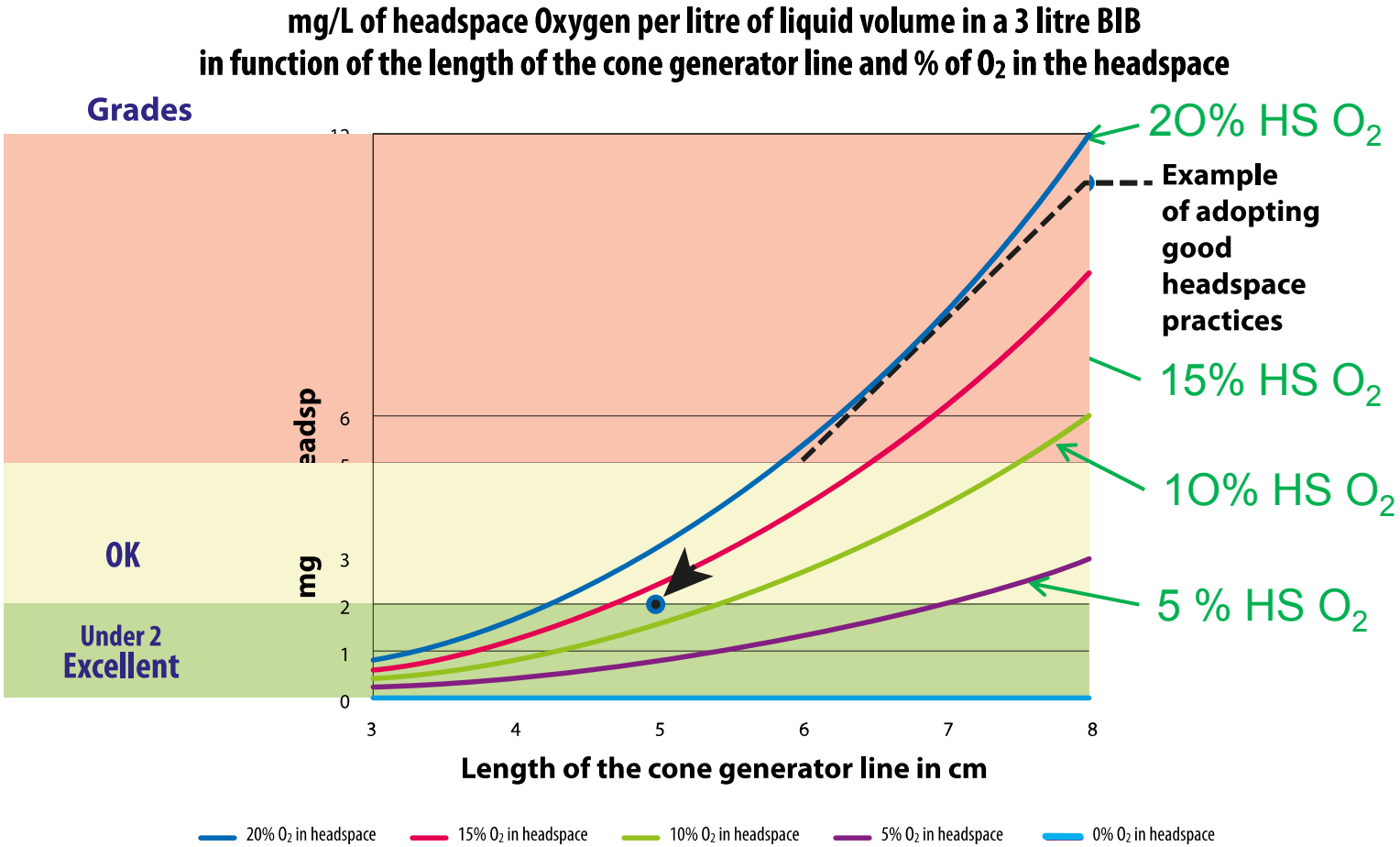
Reducing DO pickup from 1 mg/L to 0.5 mg/L

Reducing Filled package O_2 ingress from 2.5 mg/L to 2 mg/L



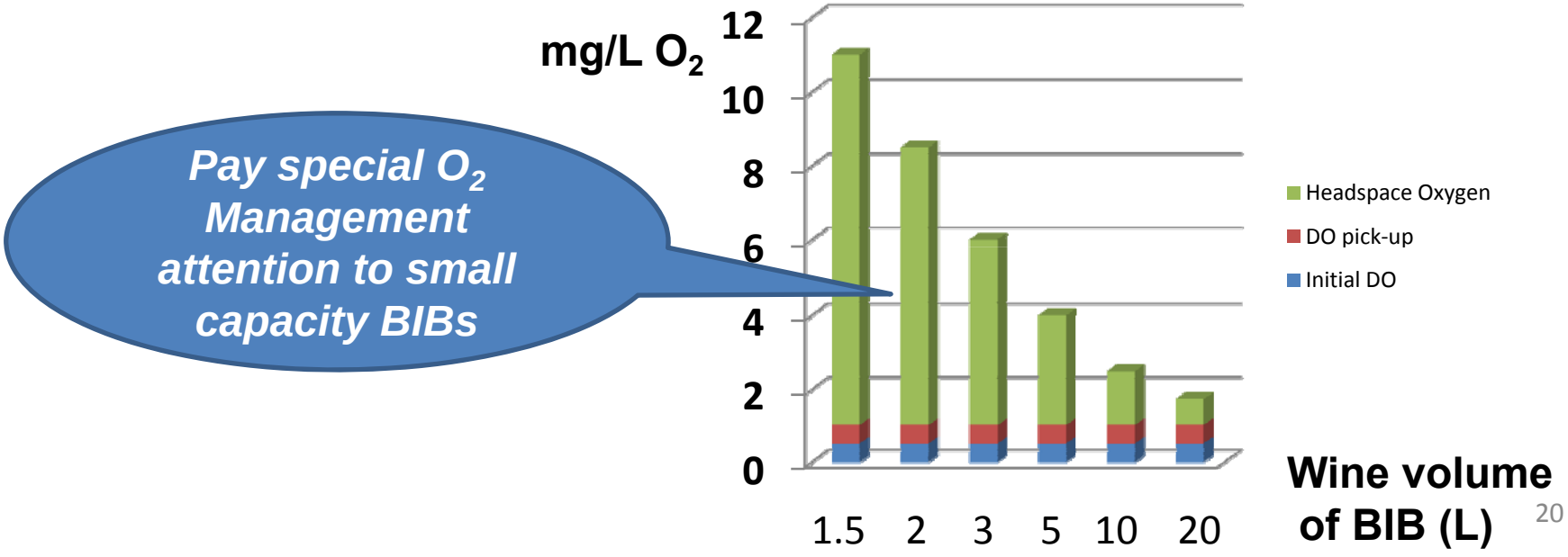
Wine BIB O_2 measurements / Part 1: Wine BIB shelf life / 1.3 The headspace problem

A graphical representation of the headspace problem



BIB size matters

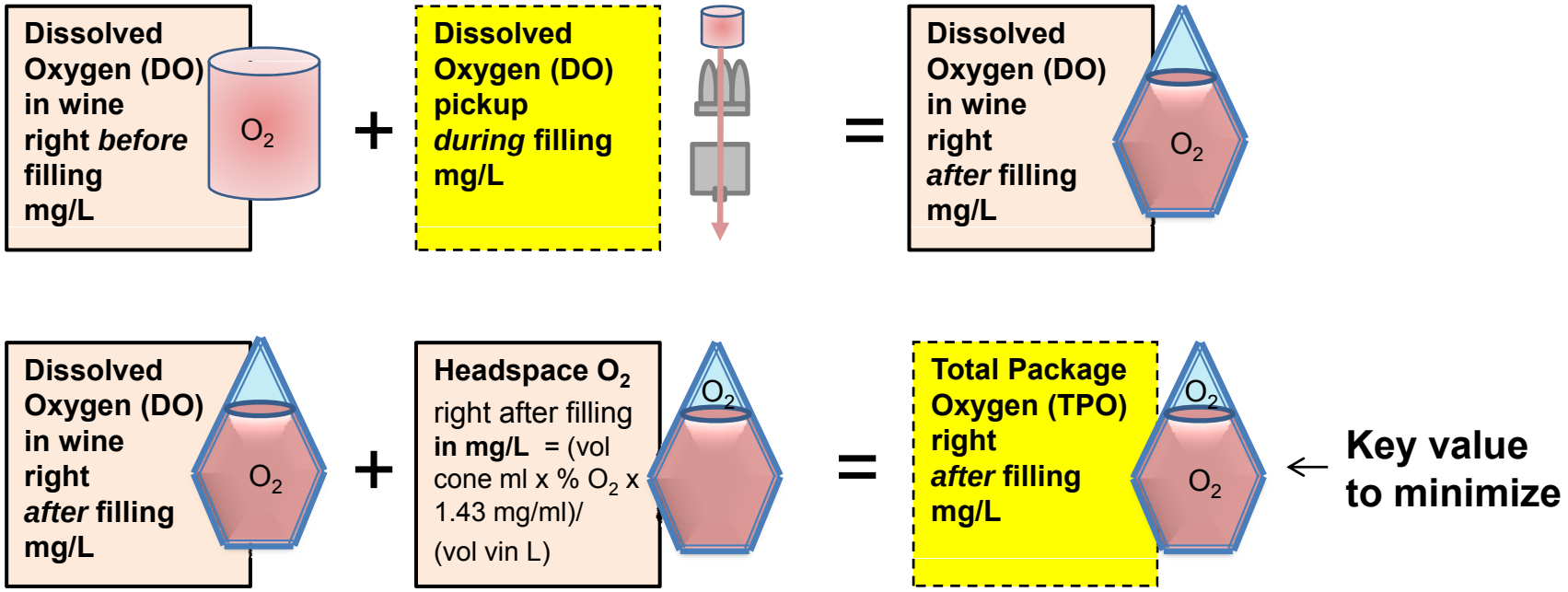
Potential Headspace oxygen problems become more acute with smaller BIB sizes. The example below assumes that the size of the air cone (headspace) and DO levels remains constant as the volume of the BIB package changes. The cone generator line is 6.5 cm and 14.9% air inside is O_2. Those packing smaller BIB sizes must manage O_2 even better and retailers pushing for 1.5 L and 2 L BIB should accept that shelf-life is likely to be shortened.



Wine BIB O_2 measurements / Part 1: Wine BIB shelf life / Annex: O_2 definitions

Definitions for key terms used in O_2 measurements

This Annex can be relevant for measurement definitions referred to relative to Current Research (part 3 of this presentation)


Dissolved Oxygen (DO) in wine right *before* filling mg/L
O_2
+
Dissolved Oxygen (DO) pickup *during* filling mg/L
=
Dissolved Oxygen (DO) in wine right *after* filling mg/L
O_2
Dissolved Oxygen (DO) in wine right *after* filling mg/L
O_2
+
Headspace O_2 right after filling **in mg/L** = (vol cone ml x % O_2 x 1.43 mg/ml)/ (vol vin L)
O_2
=
Total Package Oxygen (TPO) right *after* filling mg/L
O_2
O_2
← Key value to minimize

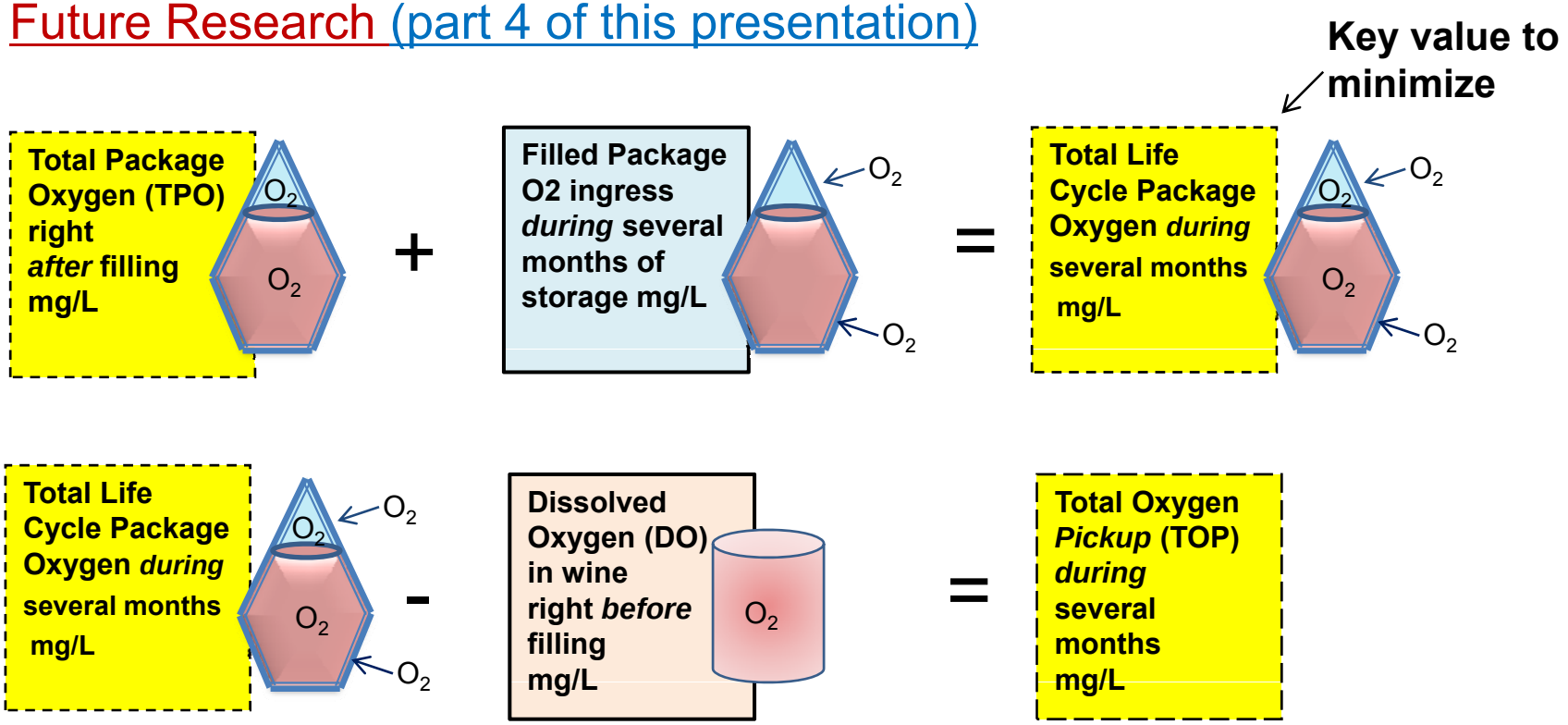
Note: Values surrounded by yellow dashed line are calculated rather than measured.

Wine BIB O_2 measurements / Part 1: Wine BIB shelf life / Annex: O_2 definitions

Definitions for key terms used in O_2 measurements

This Annex can be relevant for measurement definitions referred to relative to

Future Research (part 4 of this presentation)


Key value to minimize
Total Package Oxygen (TPO) right after filling mg/L
+
Filled Package O2 ingress during several months of storage mg/L
=
Total Life Cycle Package Oxygen during several months mg/L
Total Life Cycle Package Oxygen during several months mg/L
-
Dissolved Oxygen (DO) in wine right before filling mg/L
=
Total Oxygen Pickup (TOP) during several months mg/L
Note: Values surrounded by yellow dashed line are calculated rather than measured.

Wine BIB O_2 measurements / Part 1: Wine BIB shelf life / Annex: O_2 definitions

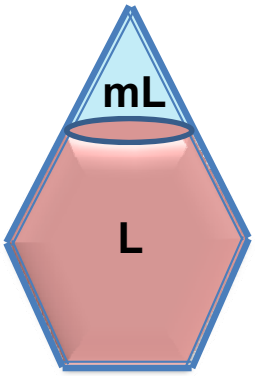
Because of the length of the definitions in the remaining pages of this Annex, it is strongly recommended that the reader go directly to Part 2 and return to this glossary of key terms only if a specific definition is sought.

Volume Definitions

Nominal liquid Volume (L): The volume stated on the label of the package (for example 3L).

Actual liquid volume (L): The true volume of the liquid in the package. For BIB wine, the actual liquid volume is supposed to be within 1.5% of the nominal liquid volume and the nominal liquid volume is often used for O_2 calculations involving volume, even if this introduces some measurement error.

Total headspace volume (mL): the volume of the gaseous (air) portion of a closed package space.



Volume capacity of the container (L): For rigid containers (such as glass bottles), the maximum capacity of the container may be a useful concept but not for BIB packaging since the maximum capacity of a BIB bag (i.e. the amount of gas or liquid that it can hold) is far in excess of its nominal volume and depends upon the particular manufacturer.

Total actual volume in package (L): the actual liquid volume plus headspace volume.

Pressure and Headspace % O_2 Definitions

Partial pressure of oxygen (hPa*): Partial pressure = total pressure x volume fraction of oxygen component. Each gas has a partial pressure which is the pressure which the gas would have if it alone occupied the volume. At 1 bar (=100 kPa = 1000 hPa) and 21% O_2, PO_2 (the partial pressure of oxygen) = 210 hPa.

Total pressure (hPa): The total pressure of a gas mixture is the sum of the partial pressures of each individual gas in the mixture. In most circumstances atmospheric pressure is closely approximated by the hydrostatic pressure caused by the weight of air above the measurement point. Average sea-level pressure is 1013.25 hPa (1 atm). As elevation increases there is less overlying atmospheric mass, so that pressure decreases with increasing elevation.

Headspace Oxygen (% O_2): % of free molecular oxygen (O_2) in the headspace gas. This can also be expressed as the ratio of the partial pressure of oxygen to total absolute pressure. For measuring instruments used to compute the % of headspace oxygen in wine packaging, the pressure generally used for the calculation (unless an adjustment is made) is external pressure. If it is suspected that the internal pressure within the package is different than the external pressure, then internal pressure should be measured and this value should be used for % calculations. For Champagne in a glass bottle the internal headspace pressure is several times the external pressure but for still wines in bag in box the internal pressure is generally very similar to external pressure. Headspace oxygen measurements for BIB packaging should be taken without applying pressure against the headspace sides during the measurements since this could introduce some error when the units are expressed in % oxygen.

* Pressure is also often expressed in kPa where 1kPa = 10 hPa

Headspace O_2 Definitions

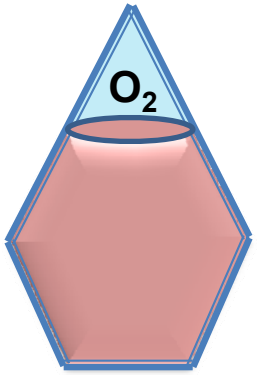
Headspace Oxygen (mL O_2): The % of headspace oxygen x headspace volume (mL)

Headspace Oxygen (mg O_2): Headspace Oxygen (mL O_2) x 1.429 mL O_2/mg O_2

Headspace Oxygen per unit of Total Headspace Volume (mg/L): Headspace Oxygen/Total Headspace Volume expressed in mg/L

Headspace Oxygen per unit of Nominal Liquid Volume (mg/L) of wine: Headspace Oxygen/Nominal Liquid Volume expressed in mg/L.

Headspace Oxygen per unit of Actual Liquid Volume (mg/L): Actual volume is to be preferred over nominal (label) volume if accuracy is sought. The headspace oxygen here can be considered as a reserve of O_2 that can potentially enter the liquid contained in the package.



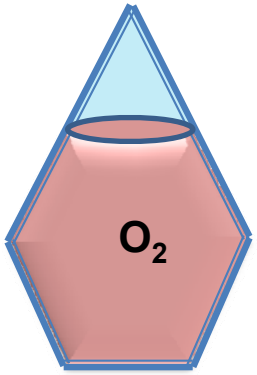
Dissolved Oxygen (DO) Definitions

DO or Dissolved Oxygen (mg/L): a relative measure of the amount of molecular oxygen (O_2) that is dissolved or carried in a unit volume of a solution . Typically, dissolved oxygen concentrations in wine are quoted in milligrams per liter (mg/L), where 1 mg/L = 1 part per million (ppm). The maximum amount of oxygen a wine can contain is around 8 mg/L at 20 ℃, which is known as the saturation level. This saturation level increases with a decrease in temperature.

DO before filling: If used for calculating DO pickup during filling, the DO level just before filling should be measured for wine in the main storage tank (or at its first exit point). Any other measurement point (during pumping, hose transport, filtration, buffer tank, etc) is to be considered as partial and should be clearly stated.

DO after filling: DO level right after filling, although, depending upon the instrument used, initial measurements may not be accurate and a stabilization time must be imposed before the DO value observed more closely reflects the true DO in the wine

DO pickup during filling: DO after filling - DO before filling (see schema page 21). This value is the result of both the positive additions of oxygen and the negative subtractions of oxygen as the wine moves through the entire process from the main wine tank (via filtration, buffer tank, etc.) to final capping in the filling machine. Although DO pick-up is generally positive, nitrogen sparging (bubbling nitrogen gas to remove dissolved oxygen from the wine) or O_2 membrane technologies could potentially result in a negative value.



General OTR and Dry Test OTR Definitions

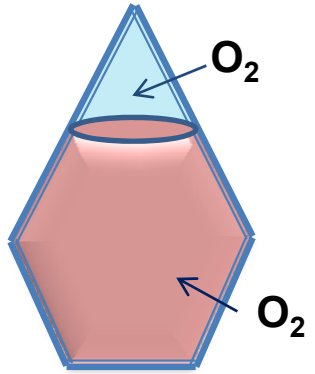
OTR (oxygen transmission rate) the measurement of the amount of oxygen gas that passes through a material (component or total package) over a given period of time.

Dry Test (gas/gas) OTR: measures the amount of oxygen that passes through a material from an outside atmosphere (generally composed of 20.95% of O_2 molecules) into an initially oxygen free chamber (flushed with nitrogen). For a "Mocon-type" test, the permeated gas is carried to a detector which is an extremely sensitive electrical-based sensor capable of detecting minute amounts of oxygen. It is also possible to use optical or florescence-based gas detection sensors but most cited references for OTR in BIB packaging are based upon electrical-based sensors. Values in metric units are generally expressed in $cm^3/m^2/24$ hr. Standard test conditions are often 73 °F (23 °C) and 50% RH but these can be made to vary.

Correlation between wine BIB shelf-life and Dry Test (gas/gas) OTR results for package components appears sometimes to be weak in part because the tests are often performed on film before being transformed into bags and filled but also because true oxygen ingress also depends on many other factors, including whether liquid is on the other side of the component (the case with BIB) and the surface contact area. Despite these limits, Dry Test (gas/gas) OTR results are very useful for industrial control purposes.

Filled Package O_2 ingress definition

Filled Package O_2 ingress* is the measurement of the amount of oxygen (in mg/L) that passes through a package filled with liquid (but also with some headspace air) during a period (days, weeks months). The outside atmosphere is generally composed of 20.95% of O_2 molecules. Generally the package is filled with high acid (to keep the micro-organisms at bay), low oxygen water and the change in the level of dissolved oxygen in the water is observed over many weeks or months. Because of oxygen initially in the headspace or embedded in the package components, a very long stabilization period (of a least of couple of weeks) is generally observed before an Oxygen Transmission Rate (OTR) is calculated. Alcohol is sometimes added to the solution (when wine is being simulated) but it should be verified that (for a particular instrument) the alcohol does not introduce measurement errors.

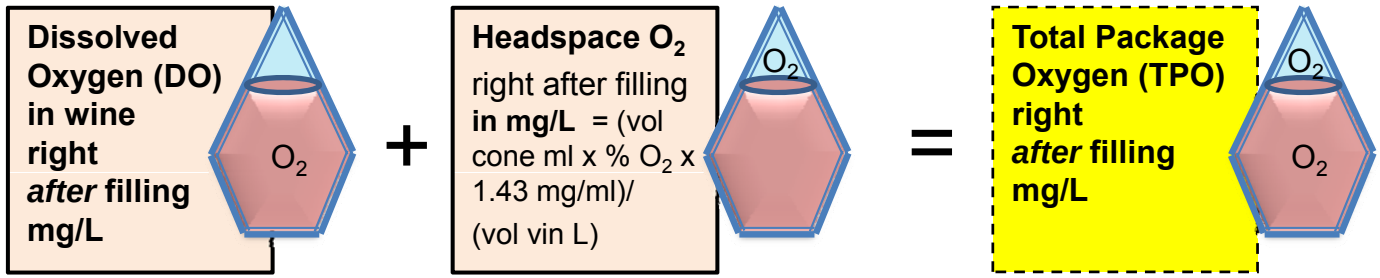


For Filled Package OTR tests, initial headspace (volume and % O_2) can be modified and package components can be sealed off (or eliminated) to see the relative contribution of this component or headspace to OTR. Changes in dissolved oxygen (expressed in mg/l or ppm) can be extrapolated to predict shelf-life but much more work must be done to interpret these curves.

* Referred to also as “Filled Package OTR”

TPO and Oxygen pickup during filling definitions

Total Package Oxygen (TPO) is Headspace Oxygen per unit of Actual Liquid Volume (mg/L) + DO in liquid (mg/L) at any given point in time, for example, right after filling. Please note that the headspace measurement value used is liquid volume rather than headspace volume. Note also that TPO observed right after filling may not include some oxygen trapped in pockets within the package or film (not yet in the liquid or headspace).

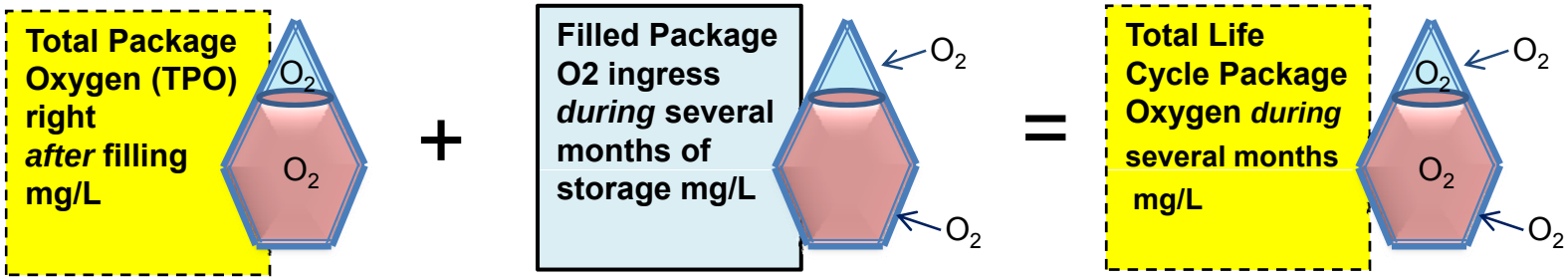

Dissolved Oxygen (DO) in wine right *after* filling mg/L
O_2
+
Headspace O_2 right after filling **in mg/L** = (vol cone ml x % O_2 x 1.43 mg/ml)/ (vol vin L)
O_2
=
Total Package Oxygen (TPO) right *after* filling mg/L
O_2
O_2

Oxygen pickup during filling is Headspace Oxygen per liter of liquid volume (mg/L) + DO pickup (DO after filling - DO before filling) in the liquid (mg/L).

Wine BIB O_2 measurements / Part 1: Wine BIB shelf life / Annex: O_2 definitions

Total Life Cycle Package Oxygen and TOP Definitions

Total Life Cycle Package Oxygen is Total Package Oxygen (TPO**)** TOP + Filled Package O_2 ingress during storage of several weeks or months. We did not find a standard expression for this value so this term has been invented. This value does not take into account the reductive-oxidative history of the wine before it is measured in the main tank before filling. Performance BIB recommends to minimize Total Life Cycle Package Oxygen, but if the wine is already nearly oxidized before filling, its shelf-life will not be very long.



Total Oxygen Pickup (TOP) is the sum of the oxygen **pickup** during filling (mg/l) + Filled Package O_2 ingress during its storage (mg/L). It is also the difference between the Total Life Cycle Package Oxygen and the dissolved oxygen (DO) in the wine before filling (see schema page 22). This covers a period of time (extending over many weeks or months) and represents the total amount of oxygen added to a beverage during the filling process and subsequent storage of the packaged product. Filled Package Test OTR (mg/L) cannot be measured with wine (because it consumes oxygen) so the oxygen pickup after filling part of TOP must be measured with a water based solution.

Part 2: Measurement technologies, by Jean-Claude Vidal, INRA

2.1) Main technologies

2.2) BIB specificities

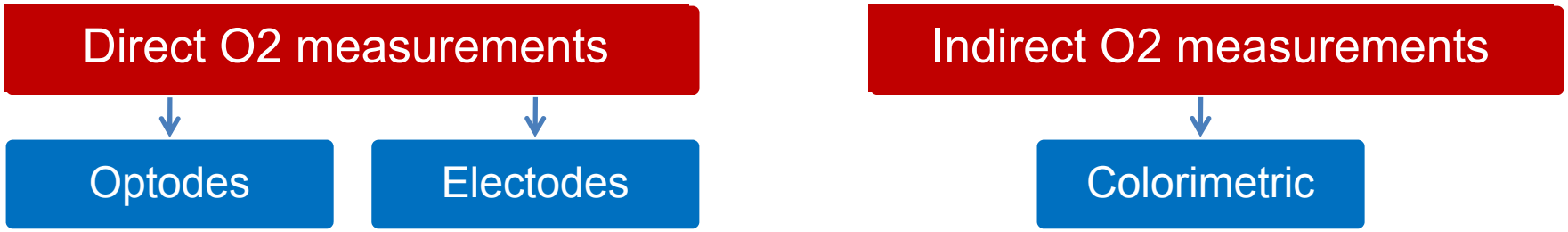
- Viewing headspace volume
- Headspace/wine ratio
- Rapidity of headspace O_2/DO mix
- Package O_2 Permeability
- BIB Headspace volume varies over time
- O_2 intake once package open

Main Oxygen measurement technologies

There are many technologies used to measure oxygen. An **oxygen sensor** is an electronic device that measures the proportion of oxygen in the gas or liquid being analyzed.

For filled wine packaging , the two main types of oxygen sensors used are **electrodes** (electrochemical sensors) and **optodes** (optical sensors). This can be used for both oxygen pickup and oxygen packaging ingress studies.

In addition to these direct measurements of oxygen, it is also possible to indirectly measure oxygen by measuring color changes in a liquid indicating oxygen ingress.



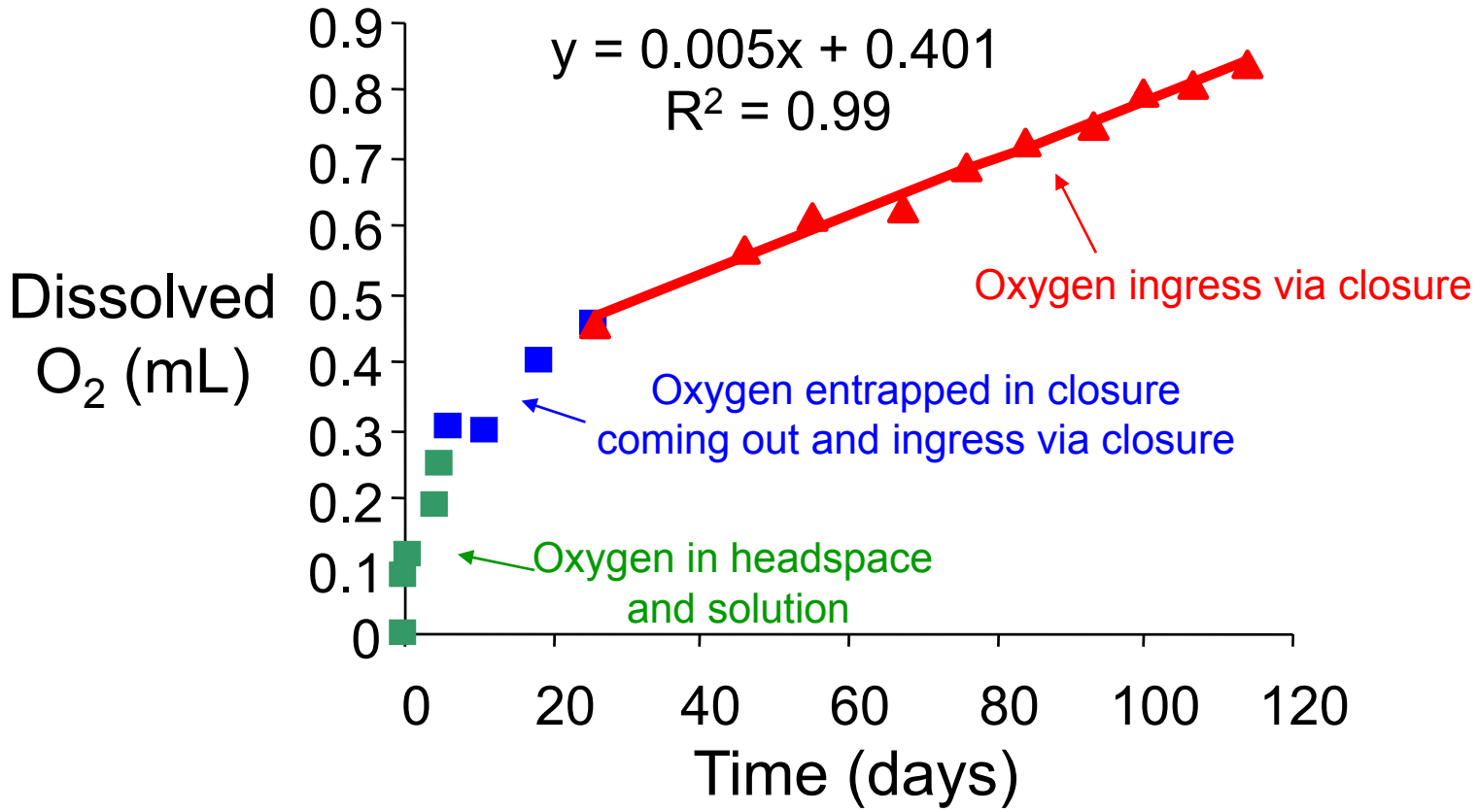
Colorimetric measure of O_2

Several colorimetric methods have been applied to wine bottles, but to our knowledge, none so far to BIB packaging. These techniques are used for wine packaging to measure oxygen ingress rather than oxygen pickup during filling.

- **Ribereau-Gayon's indigo carmine method**, based on the color change from the oxidation-reduction reaction of indigo carmine.

- **AWRI's BPAA method** using two reagents in a model wine: BPAA as an oxygen trap and methylene blue and light as a sensitizer.

Example of BPAA colorimetric method applied to wine bottle OTR



Source: Skouroumounis et al (2007) AWITC.

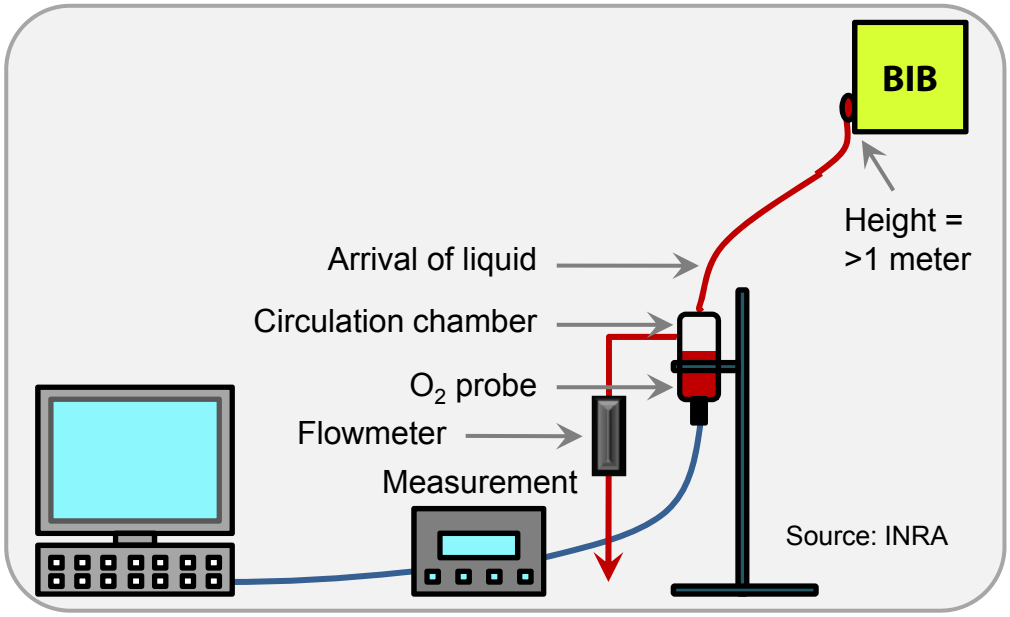
The graph above was presented by Mai Nygaard at the 26 November 2007 Performance BIB meeting in Nîmes

O_2 electrodes

The Clark-type electrode is a very commonly used oxygen sensor. Molecular oxygen passes trough a permeable membrane creating a measurable electrical current and the intensity of the current rises with a rise in the partial pressure of the oxygen PO_2

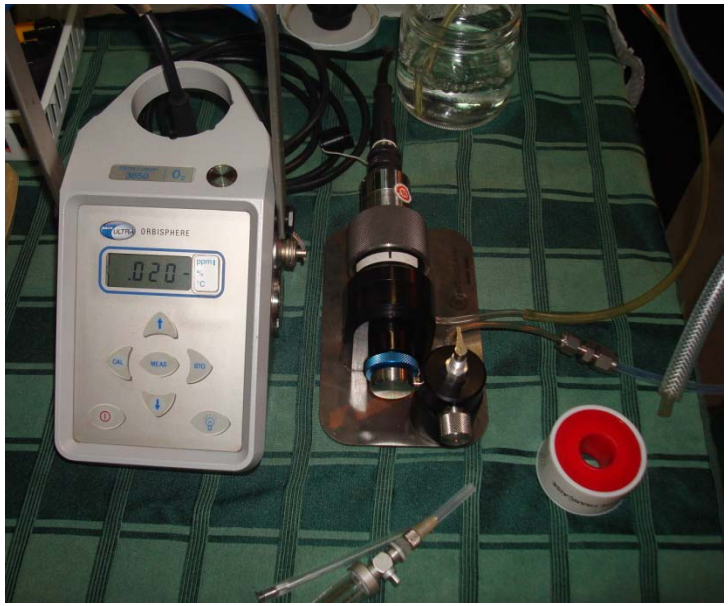
O_2 electrodes ➔ DO

Examples of the measurement of DO in wine with an electrode.



O_2 electrodes ➔ Headspace

Electrodes can also be used to measure headspace oxygen



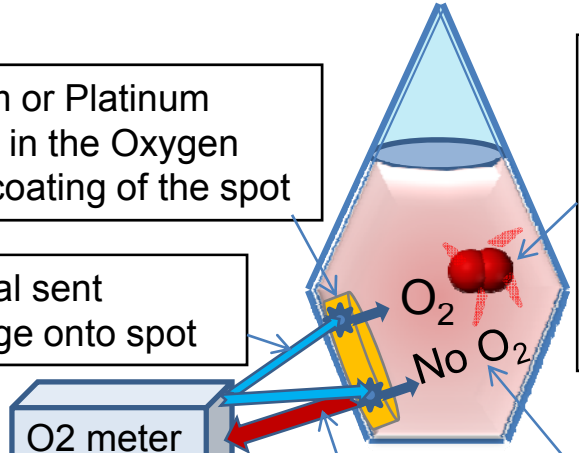
O_2 optodes: How does it work?

Blue light from LED is transmitted through transparent packaging to the surface of sensor spot, where it is absorbed by platinum or ruthenium molecules

In the absence of oxygen the platinum or ruthenium molecules will emit red light, which is detected by the optode. **The average time between the absorption of the blue light and the release of the red light allows for the calculation of the oxygen content**.

Ruthenium or Platinum molecules in the Oxygen sensitive coating of the spot

Blue LED signal sent through package onto spot

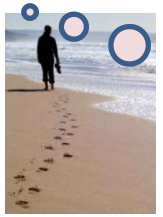


If excited Ruthenium or Platinum molecules transfer energy to O_2 mate, then little or no red fluorescence signal is sent back to detector

O2 meter

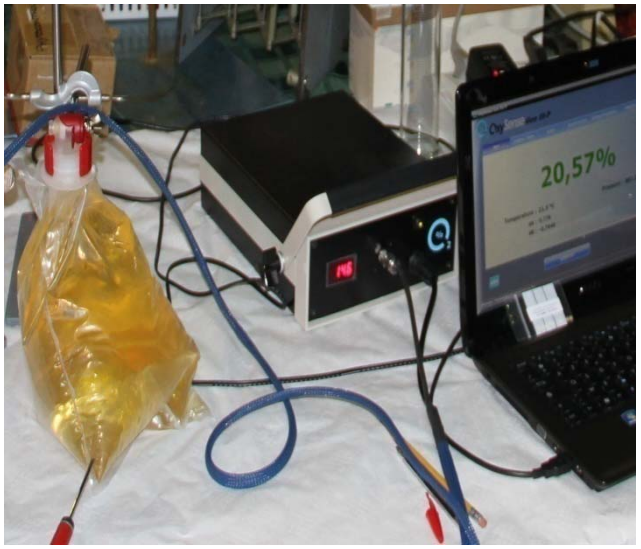
Box with hardware and software to calculate O_2 content based delays of light signals.

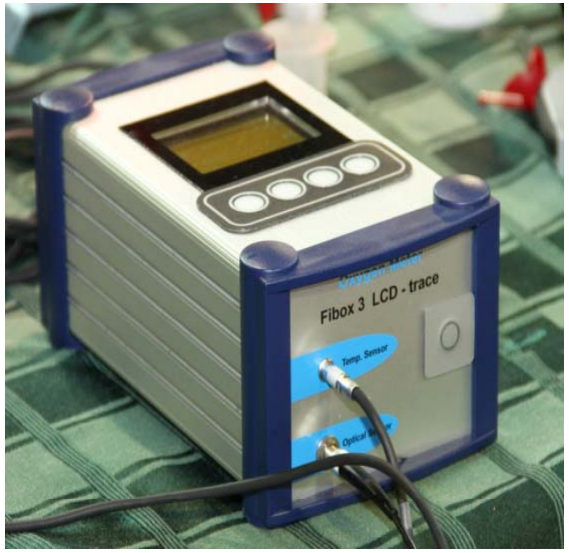
If the excited Ruthenium or Platinum molecules remain alone there is no energy transfer to O_2 molecules and red light is sent back to detector



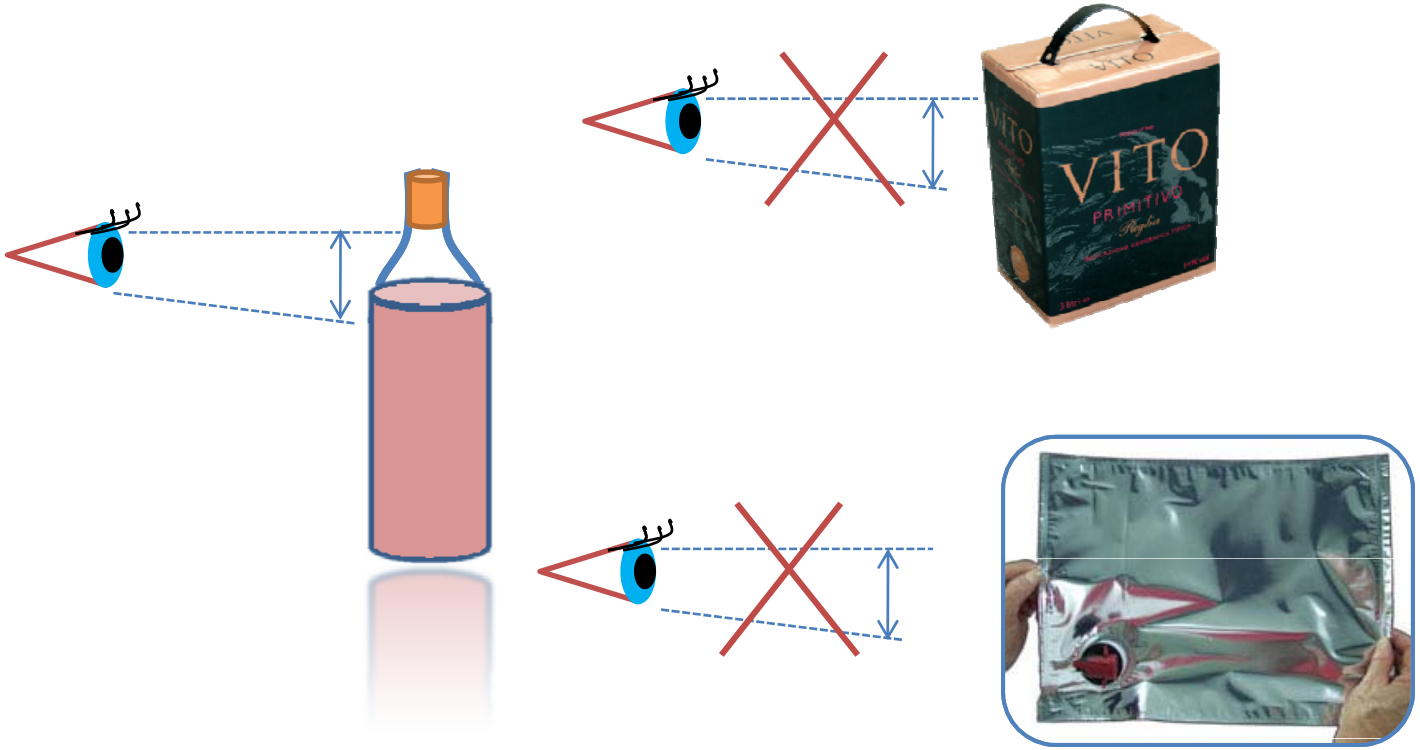
O_2 Where are you?

Optodes





Bottle headspace easier to see and measure than BIB



Bottle vs BIB headspace

% of headspace relative to wine volume for bottle and BIB packaging

Headspace volume (mL)		Wine volume (L)				
		Bottle	BIB			
		0.75	1.5	3	5	10
Cork	5	0.7%				
Cork	9	1,2%				
Screwcap (Bottle)	14	1.9%				
Screwcap (Bottle)	65		4.3%	2.2%	1.3%	0.7%
Screwcap (Bottle)	100		6.7%	3.3%	2.0%	1.0%
Screwcap (Bottle)	400		26.7%	13.3%	8.0%	4.0%

Length of BIB cone generator line

← 6.3 cm

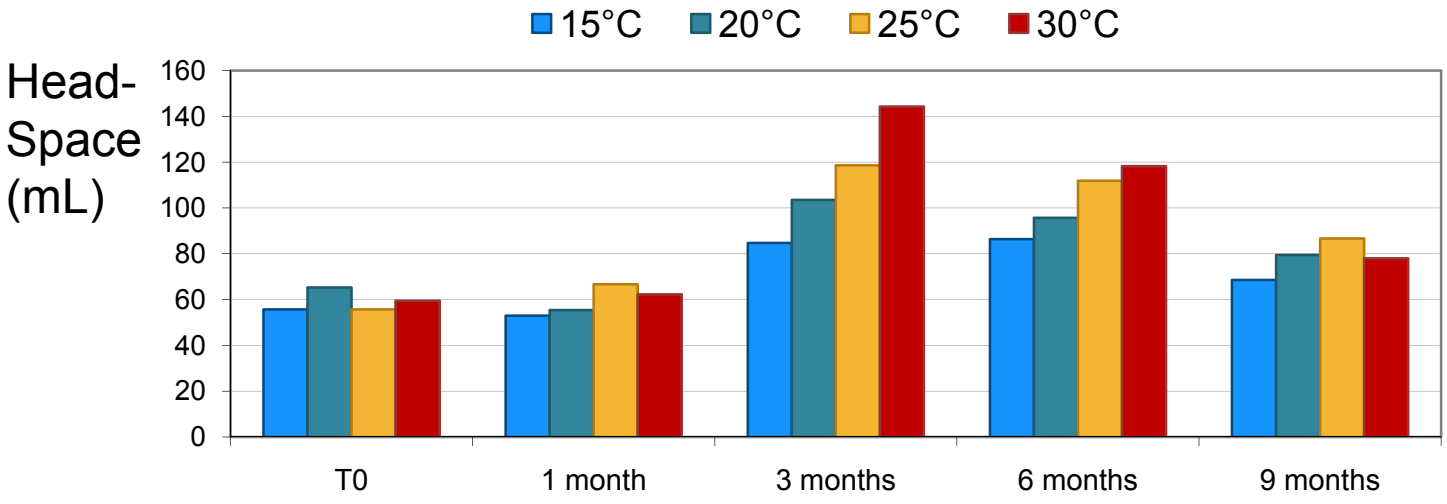
← 7.4 cm

← 12.0 cm

BIB headspace volume varies over time

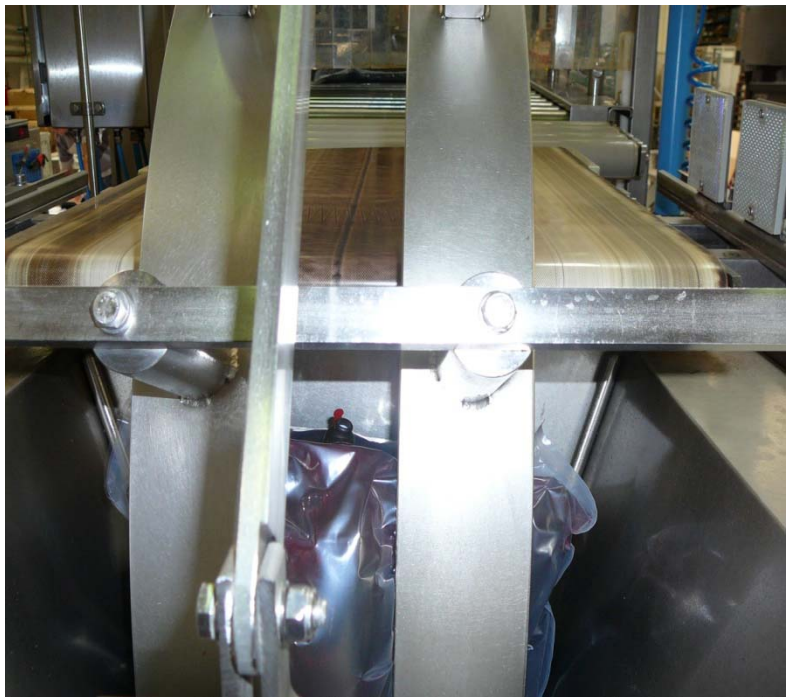
Gases that were dissolved (such as CO_2) can come out of wine in gas form, adding to the bubble (air cone) inside the bag. It is thought that after 3 to 5 months the amount of CO_2 permeating from the air cone out through the package will be greater than the CO_2 coming out of solution and the size of the air cone will begin to decrease.

Below are the results of the 2004 INRA study for Performance BIB which showed the headspace volume (mL) in function of storage temperature over a nine month period.



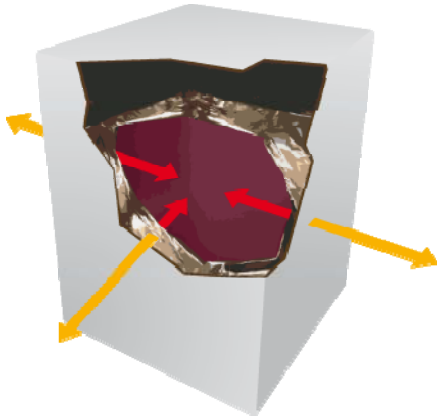
Bottle headspace mixes less rapidly than BIB headspace

O_2 in BIB headspace mixes more quickly with the wine because the bag falls more violently into the box than bottles being placed into boxes on the filling line.



Glass bottles are less permeable to oxygen

Flexible BIB package is more permeable to oxygen than glass as oxygen can enter in through the film, the closure and weld interfaces.



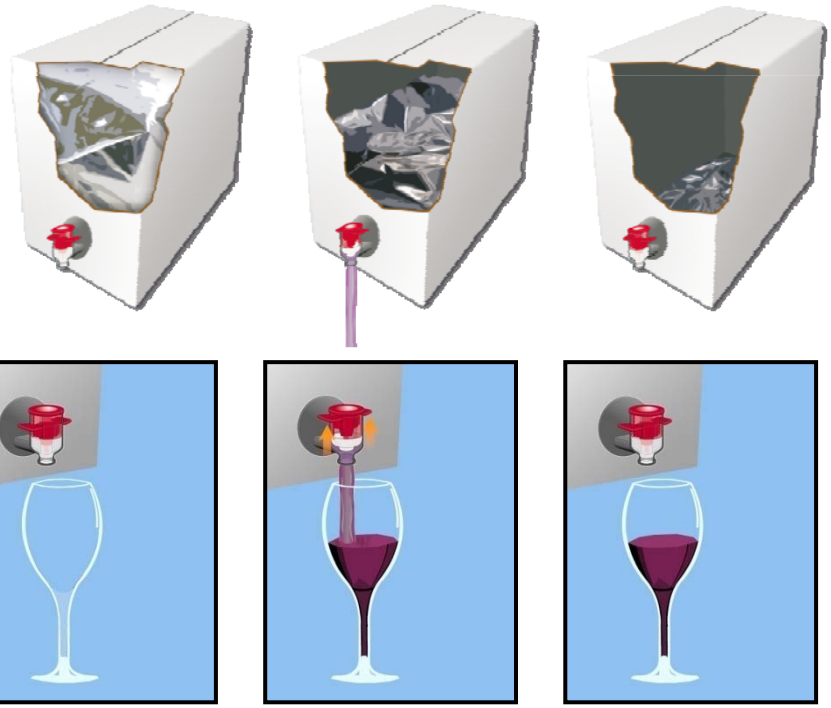
For a glass wine bottle, zero oxygen enters in via the glass and the permeability is essentially linked to the closure with oxygen going into the wine:

- directly through the closure
- through the closure/glass bottle interface
- which is released from within the closure itself

Less O_2 intake in BIB once opened

As wine is poured from a filled BIB the flexible film collapses around the wine and no air enters during the pouring process. For most BIB taps, closure after use is automatic and the wine inside will stay fresh for several weeks after opening.

For glass bottles, PET bottles, beverage cartons and aluminum cans, once the closure is opened, air enters the package and shelf-life is considerably reduced. Closure after use is manual rather than automatic.



Part 3: Recommended Procedures, by Sophie Vialis, Inter-Rhône

3.1) Problems & solutions

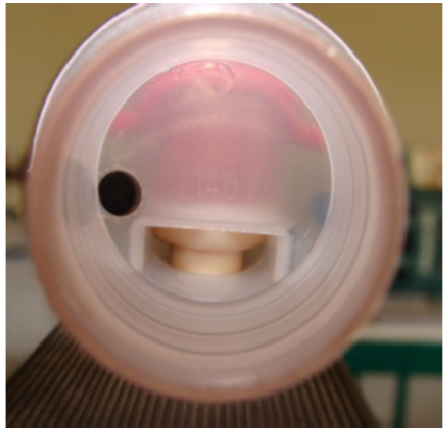
3.2) Measure Headspace volume

3.3) Headspace O_2 and DO

The Performance BIB O_2 measurement project context

1st problem: For optical measurements, find a better way to maintain the sensor spots inside the BIB since they come unstuck when glued to flexible PE film. It was also important to avoid introducing a lot of air into the bag while gluing the spot, to avoid making a hole in the bag (when fixing a viewing window, for example) and to keep as close to realistic fill conditions as possible.

Solution: Use of a transparent Vitop tap with spot glued inside tap to measure wine or headspace oxygen after filling the BIB.



The Performance BIB O_2 measurement project context

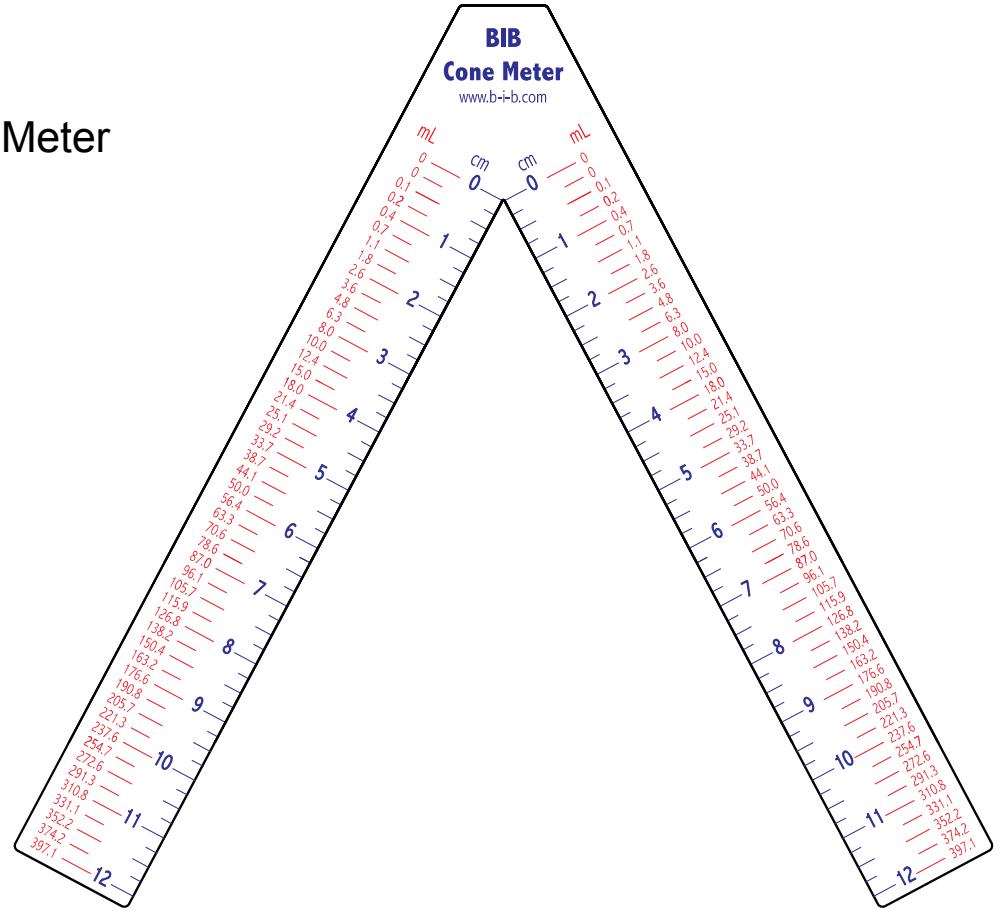
2nd problem: Standardize O_2 measurement protocol after filling

Solution: Conduct both lab and field tests and suggest protocol based upon experience

The Performance BIB O_2 measurement project context

3rd problem: Increase the precision and simplicity of the the measurement of headspace volume

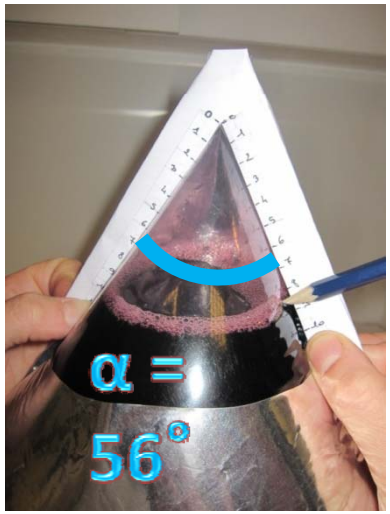
Solution: Creation of the Bib Cone Meter

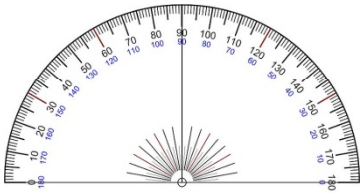


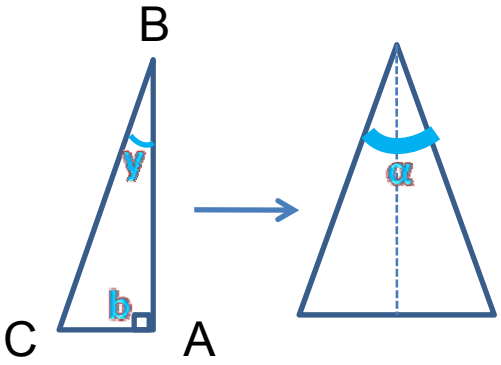
The birth of the BIB cone meter

1st stage: Determination of the true angle of the air cone in a filled BIB package

This was done by developing a protoype cone meter that exactly fit the angle created by the two sides and then measuring the angle with a protractor. This was further verified mathematically. The true angle is very close to 56°





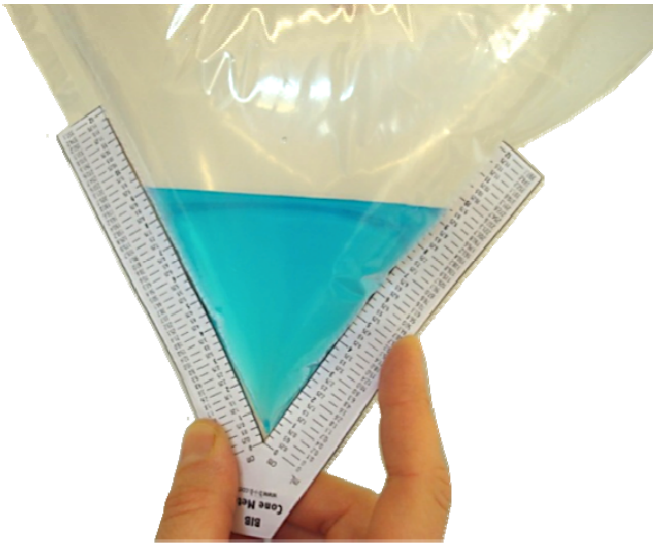


If AB = 5.3, CB = 6 and angle b = 90° then
angle y = 27.95° and
α = 2 y = 55.90°

The birth of the BIB cone meter

2nd stage: Determination of the relationship between the length of the cone generator line and the volume of the air cone (headspace)

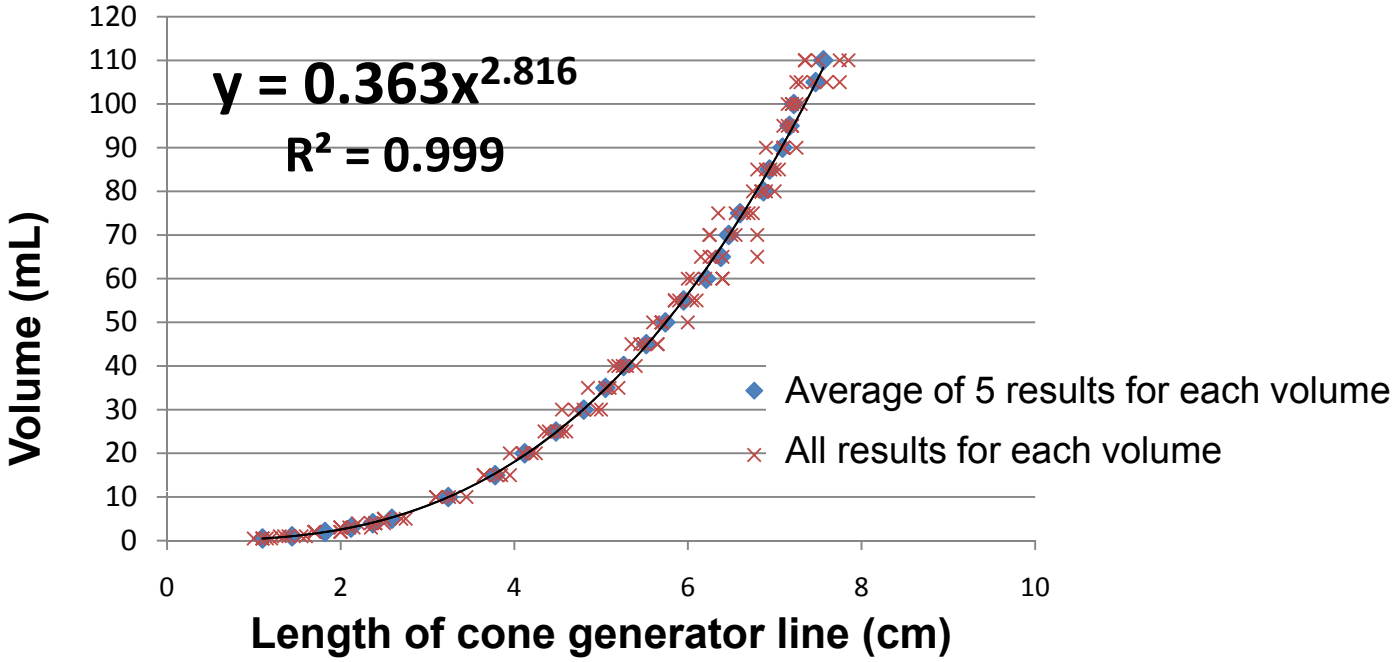
This was done by adding a pre-determined quantity of liquid into the bag (for example 50 mL) and reading out the length of the side of the cone generator line (for example 5.75 cm) for a wide range of liquid volumes. This was repeated for several nominal volumes.



The birth of the BIB cone meter

3rd stage: Establishing a power equation to express the correlation

This was done on the basis of all the real results gathered in stage 2

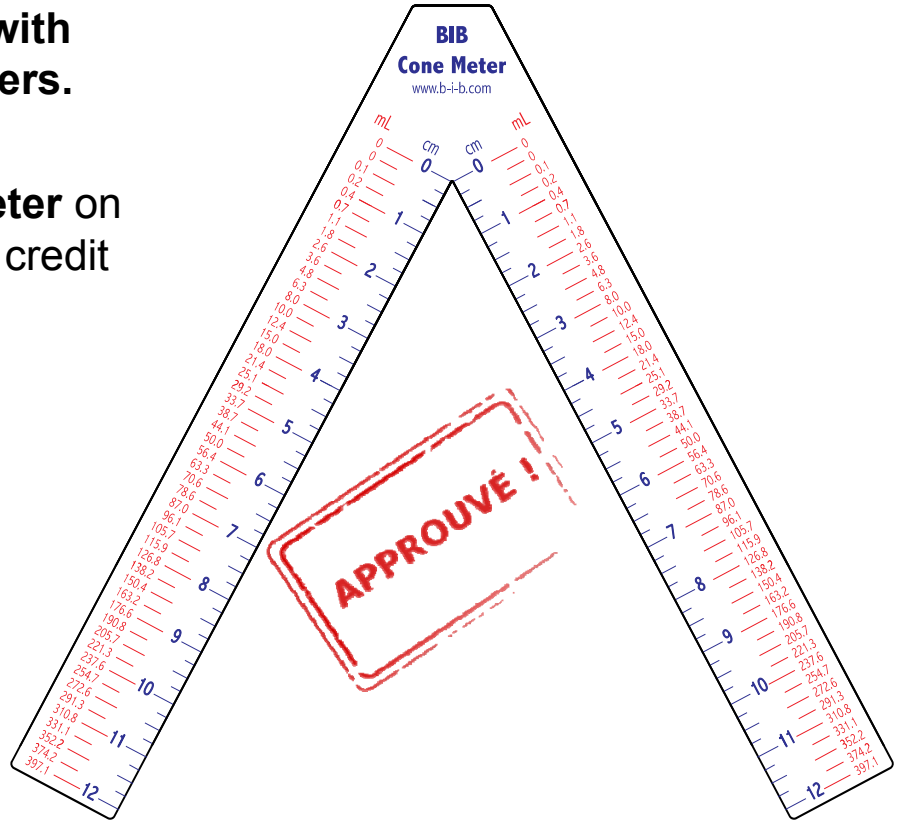


4th stage: Setting an upper limit: 12 cm max. (almost 400 mL of air!)

The birth of the BIB cone meter

5th stage: Validation of BIB bags of different nominal volumes (1.5 to 20L) with bags from several different manufacturers.

6th stage: Printing of the BIB Cone Meter on a plastic support (about the thickness of a credit card).

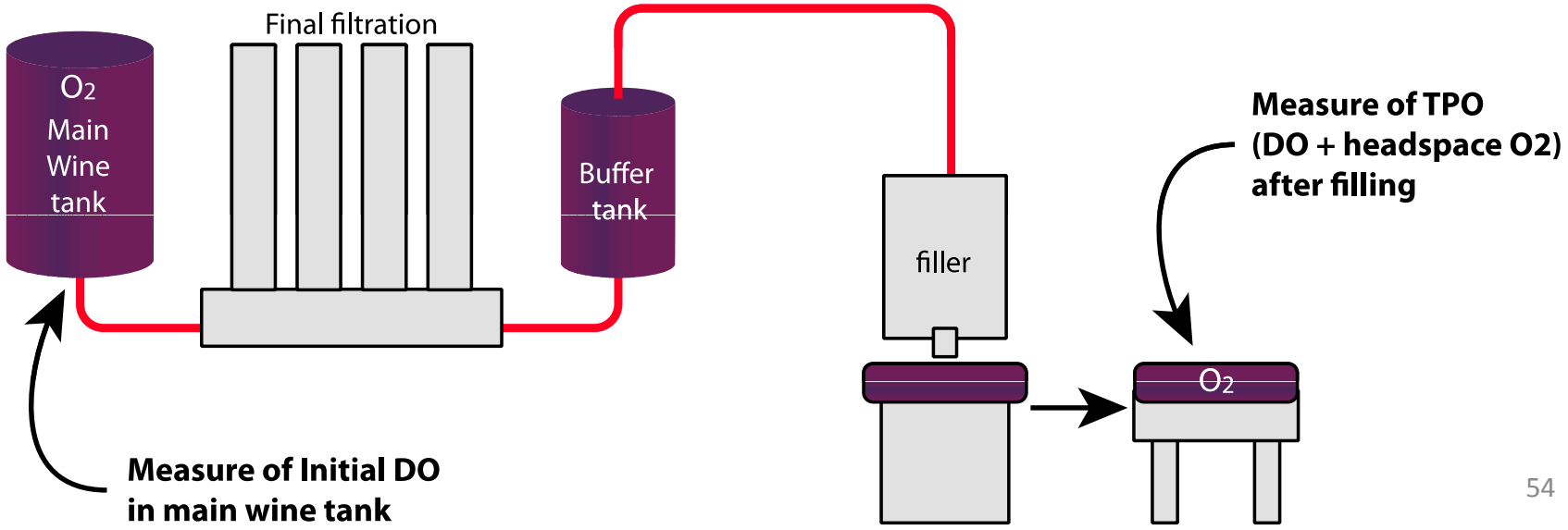


At what points are oxygen pickup measured?

Oxygen pickup is measured between two points in the filling process

We suggest that BIB wine O_2 pickup during filling be defined as the difference between the Total Package Oxygen (TPO) of the filled BIB (very close to the filler) and the initial DO of the wine in the main tank (or close to it).

Other points in-between (before and after filtration, exit buffer tank, entry filler, BIB still held by gripper jaws of filling machine etc.) may help identify pickup sources but these represent only partial pickup points. It is important to agree on terms!



Be prepared

It is preferable to use transparent bags for O_2 tests since visual control of headspace is much easier with transparent bags. For both optical and electrochemical measurements, the winery should refer to the user manual for guidance. For optical measurements it is also recommended to:

- **Use a transparent tap** as a support for the sensor spot and preferably a tap which has been modified so that it can be removed from its gland after the measurement has been taken and used (with its glued spot) for other tests.

- **Verify that the sensor spots have not exceeded their date or use limits.**

- **Glue the sensor spot several hours before use,** choosing a place on the inside of the tap which is accessible (from the outside of the tap) by the optical cable.

- **Store the spots (or taps with spots) away from light.**

Test wine bags should be clearly identified as not for commercial use.

Calibration

For all O_2 measurement technologies, proper calibration is recommended to increase precision.

For optical technologies, there are two sources of obtaining calibration values:

First option is to use the values supplied by the manufacturer for each lot of sensor spots delivered.

Second option is for the user to perform calibration, taking into account local conditions to increase precision.

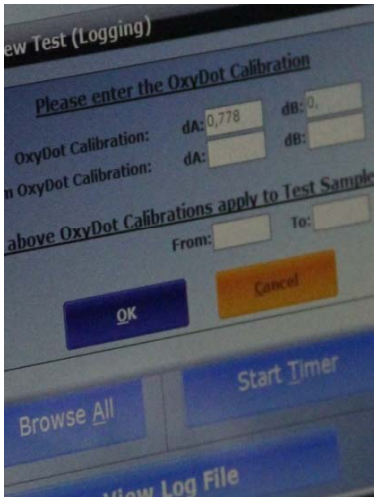
The values for the first option are determined under the laboratory conditions of the manufacturer (not taking into account the aging of the spots, the support upon which it is glued, the length of the optical cable used, etc.). A calibration by the user allows for an adjustment to these local conditions.

It is good practice to maintain a traceability of spots (and taps having specific spots glued to them) and their calibration values, and to enter their right calibration values for each new test with an optical instrument.

Calibration

Calibration is performed generally with two points: for example at 0 % oxygen (low point) and 21% oxygen v/v (high point).

The user can either apply the instructions of the manufacturer or develop their own calibration method. The easiest (for the low point) is to create 0% O_2 in a small chamber which can be in part the tap itself, held open (for nitrogen flushing) by a connector.



Initial DO measurements in the main wine tank*

There are three main sampling techniques:

-**Inside the tank:** A dipping probe can be fed into the tank from above, with measurements at the bottom, the top and the middle of the tank to test homogenity and to obtain an average value.

- **At the tank main exit:** For optodes, a sensor spot can be glued on a transparent glass window one one of the connection links at the exit of the wine tank. If a glass window is used, it should be transparent and not too thick (< 12 mm). If the wine is too cold, condensation on the glass can prevent the correct measurement from being taken. Some optodes (with integrated sensor spots) require a liquid circulation chamber connected to the exit of the main wine tank.

For electrodes, wine can be drawn into the instrument (from a deviation link placed in the exit hose) and measured.

- **Draw a sample from the tasting tap**. For optodes, the wine can be placed in a small glass recipient (fushed previously with inert gas) with a sensor spot. This method is not recommended if other options are available. For electrodes, the measurement can be taken by directly making the wine flow from the tasting tap.

* By main wine tank, we mean the main tank used for filling, before final filtration and any buffer tank.

Initial DO measurements directly into the main wine tank

The in-tank dipping method for opical measurements: Dipping probe fed into the tank from above or via a side tank (shown). It is best to stir the probe while it is the tank to decrease stabilisation time.

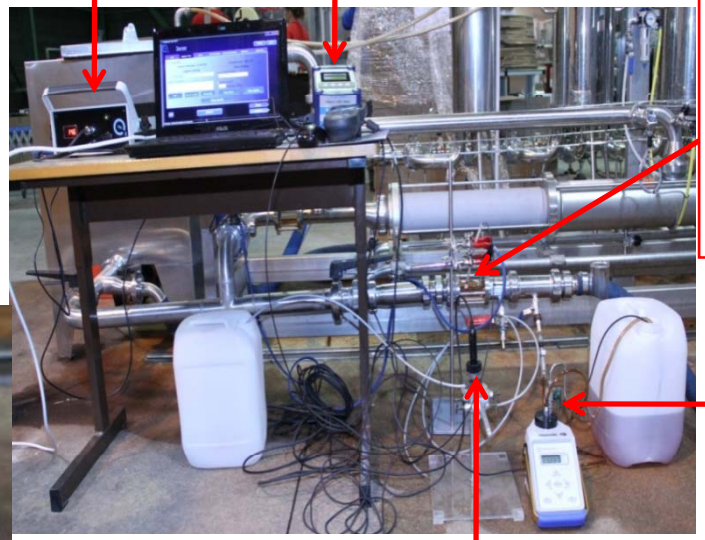
Initial DO measurements exit from the main wine tank

This can be conducted directly at the exit of the main wine tank with an optical instrument. For some optical technologies, a sopt can be glued on the other side of a transparent window to allow this measurement to take place..

Initial DO measurements exit from the main wine tank

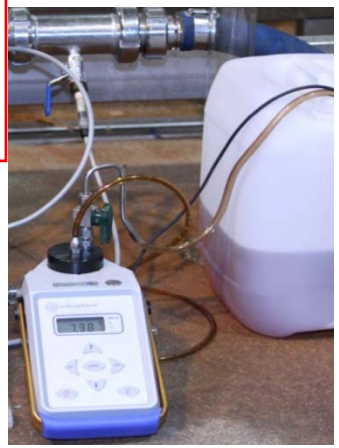
Results from several measurement technologies can be compared at the same point of exit.

2 optodes



Transparent window with spots for optical measurements

Flow unit for electro-chemical method



Circulation chamber for optical measurement with integrated spot

TPO measurements after filling

For all measurement technologies it is not easy to take the first measurement (after filling and capping) while the wine BIB is still held by the grippers of the filling machine.

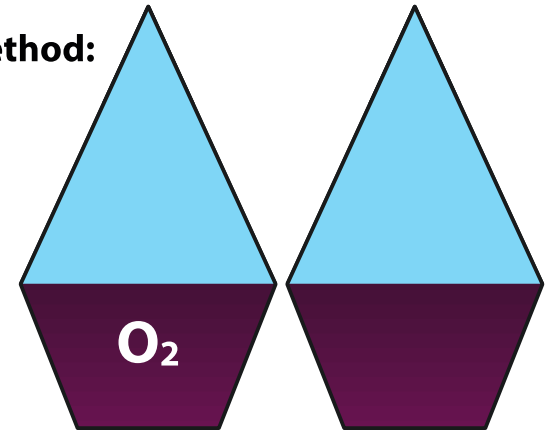
For this reason it is recommended to take the BIB sample **right after it has been filled and tapped** but to gently catch it as soon as it is released by the grippers but before the bag has fallen into the box. This generally implies that the machine must be temporarily stopped when the sample is taken.

When the BIB is taken, it should be **gently transported (holding the tap on top)** to a test table located close to the filling machine. The BIB should be readied first for headspace analysis (for optical measurements) without mixing the wine.

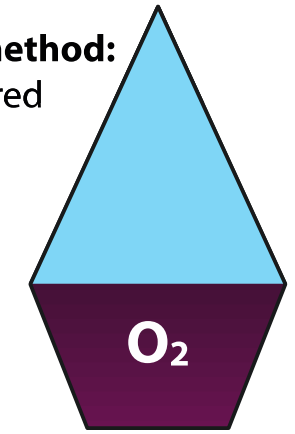
TPO measurements after filling

Because the same sensor spot can be used for headspace oxygen and for DO (by reversing the position of the BIB), there is a need for only one BIB for each optical sample set.

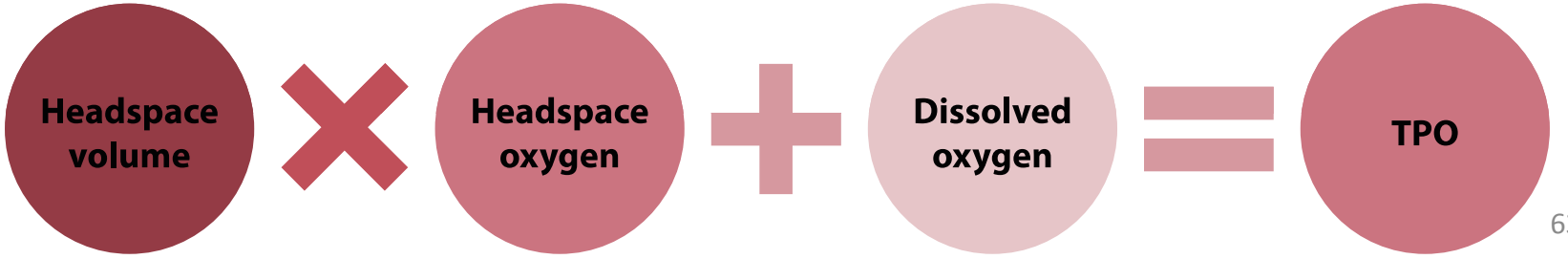
For the electrochemical method:
2 BIBs are required



For the optical method:
1 BIB is required



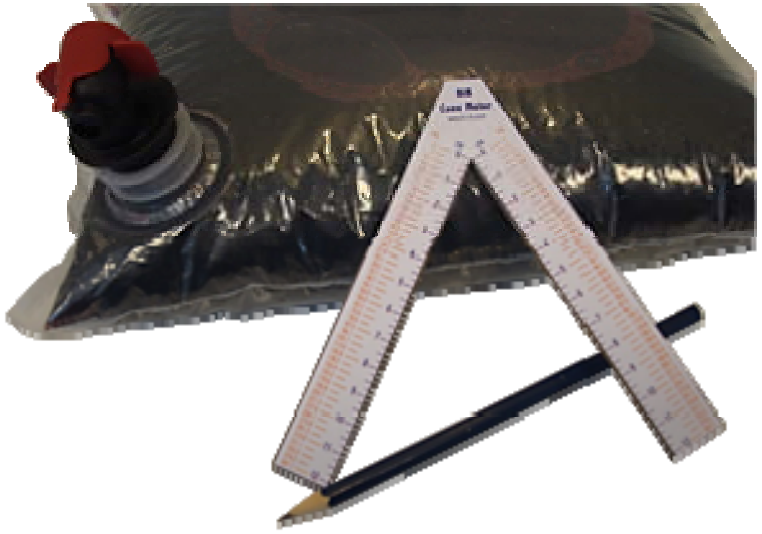
To determine TPO, 3 measurements must be taken:



Measuring headspace volume

- Prepare an ample work space with cone meter
- For optodes: calculate headspace volume right after headspace oxygen has been measured and just before the DO measurements for the wine.
-For electrodes: measure headspace volume before headspace oxygen.

- Squeeze the headspace air gently into the form of a cone



Measuring headspace volume

Position the BIB Cone Meter and measure the two sides of the cone (in cm)

Calculate the average in cm and read the corresponding volume of the cone in mL from the BIB Cone Meter.

ml	cm
44.1	5.50
50.0	5.75
56.4	6.00
63.3	6.25
70.6	6.50
78.6	6.75
87.0	7.00

Abracadabra!

Measuring headspace volume

For the special case of metallized bags,

remove the outer metallised film layer with the help of a cutter and a pair of scissors – preferably without piercing the bag!

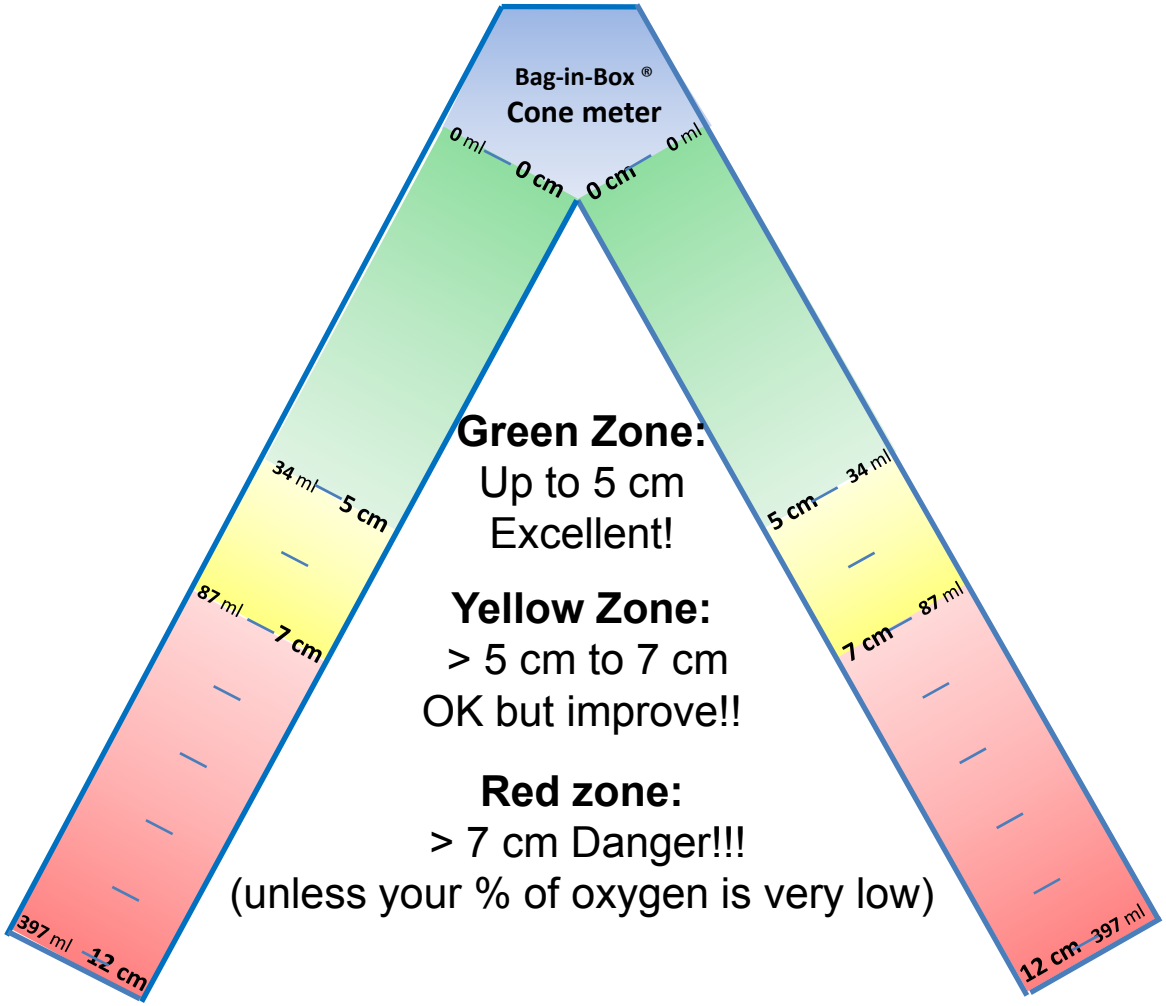
Measuring headspace volume

For the special cases of bags:

- with rounded corners (welds), measure the full cone to the apex and then deduct the volume of the missing corner (generally < 2 mL)

- filled with a lot of foam, preferably wait for the average foam thickness to settle under 5 mm and then measure from the bottom of the foam. Alternatively subtract from the total headspace (measured from the bottom of the foam) the liquid equivalent of the foam. This liquid equivalent is calculated by estimating the volume of the foam (using the cone meter) and multiplying the foam volume by a coefficient (we use 15%).

A simple rule of thumb using the BIB cone meter



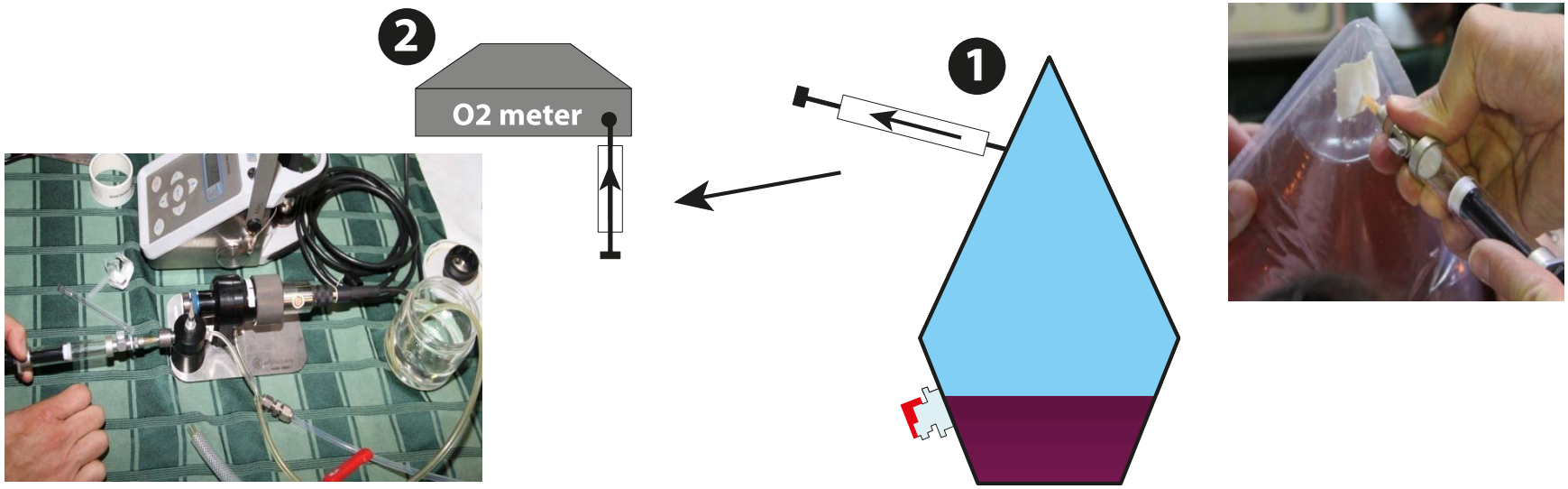
Green Zone:
Up to 5 cm
Excellent!

Yellow Zone:
> 5 cm to 7 cm
OK but improve!!

Red zone:
> 7 cm Danger!!!
(unless your % of oxygen is very low)

Measuring headspace oxygen with electrodes

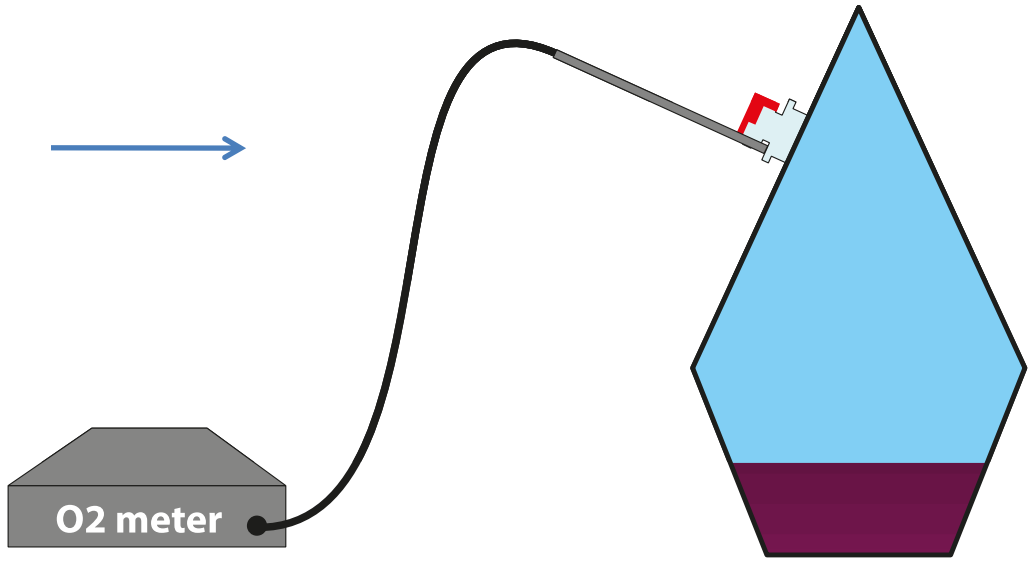
- Place some tape on the aircone in the spot where it is to be pierced.
- Pull an air sample slowly into a syringe and inject immediately (but slowly) into measurement chamber for % O_2 reading.
- there is an underlying hypothesis that the internal pressure of the BIB aircone is similar to the pressure inside the measurement chambre but this is probably the case for BIB.



Measuring headspace oxygen with an optode

Using optical instruments:

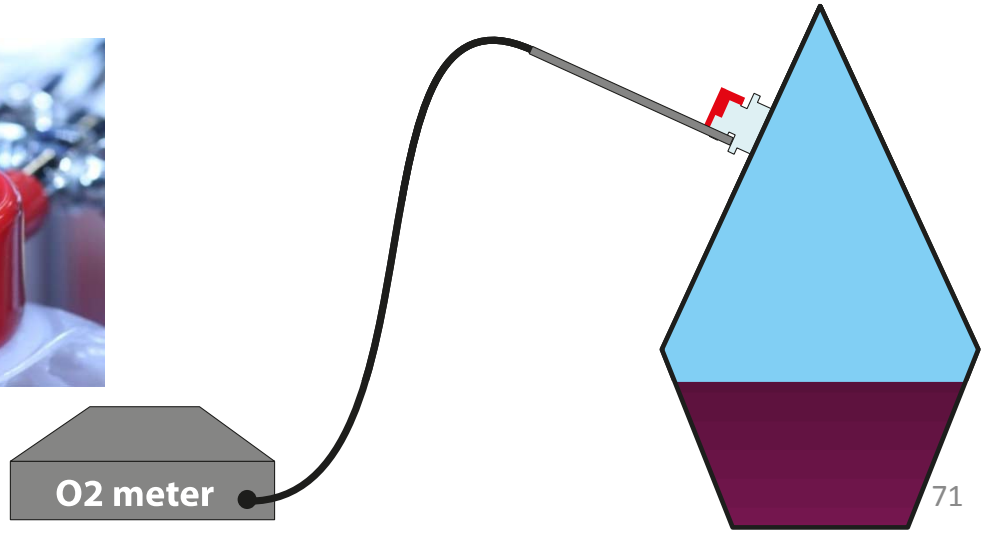
- Carry the BIB gently from the filling machine to a measurement table located as close as possible to the filling machine
- For the measurement, secure the BIB (with the tap above) with the help of a holding clamp
- Make the measurements immediately after filling



Measuring headspace oxygen with an optode

Using optical instruments:

- We consider the values to be acceptably **stabilized within 2 minutes** for most situations
- **Record the oxygen result in %.** The simplicity of using a value in % could be a source of error if the total pressure inside the package was very different than the total pressure used for the calculations (by the optode) but this is generally not the case with BIB packaging.



Calculate headspace oxygen in mg/L

After having measured the % of oxygen in the cone using an oxygen sensor (= % O_2):

Calculate the quantity of oxygen in the cone (mg/L) using the following formula:

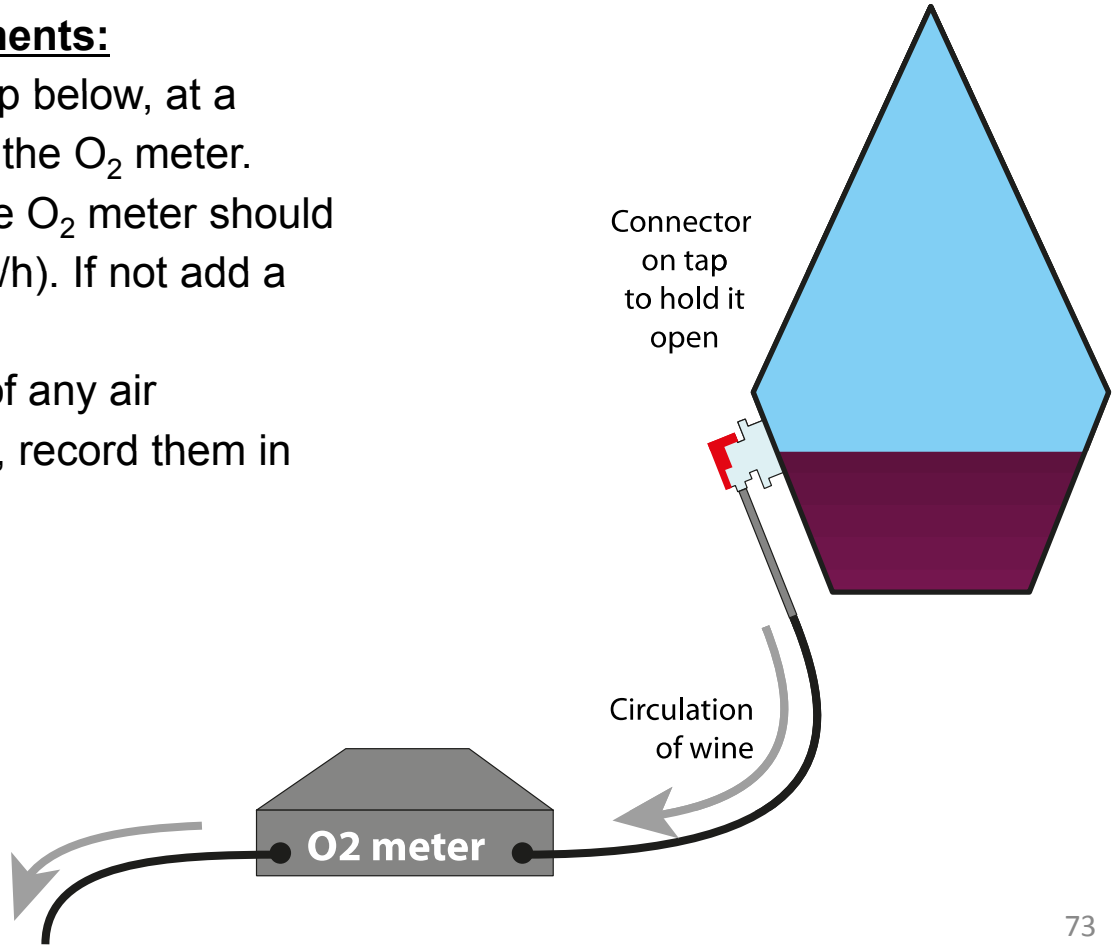
$$\frac{(\%\ O_2) \times (\text{volume headspace mL}) \times (1.429\ \text{mg}\ O_2/\text{mL}\ O_2)}{\text{volume BIB (L wine)}}$$

The result is an expression of the reserve of O_2 in the cone that could potentially be transferred to the wine.

Calculate DO with electrodes

Using electrochemical instruments:

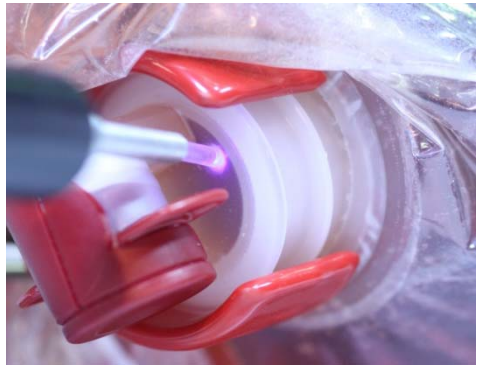
- Put the BIB in a box with the tap below, at a height of about 1 meter above the O_2 meter.
- The debit of the wine exiting the O_2 meter should be regular and sufficient (10 L/h). If not add a peristaltic pump after O_2 meter.
- Wait until the circuit is purged of any air
- When the measures are stable, record them in ppm (mg/L)

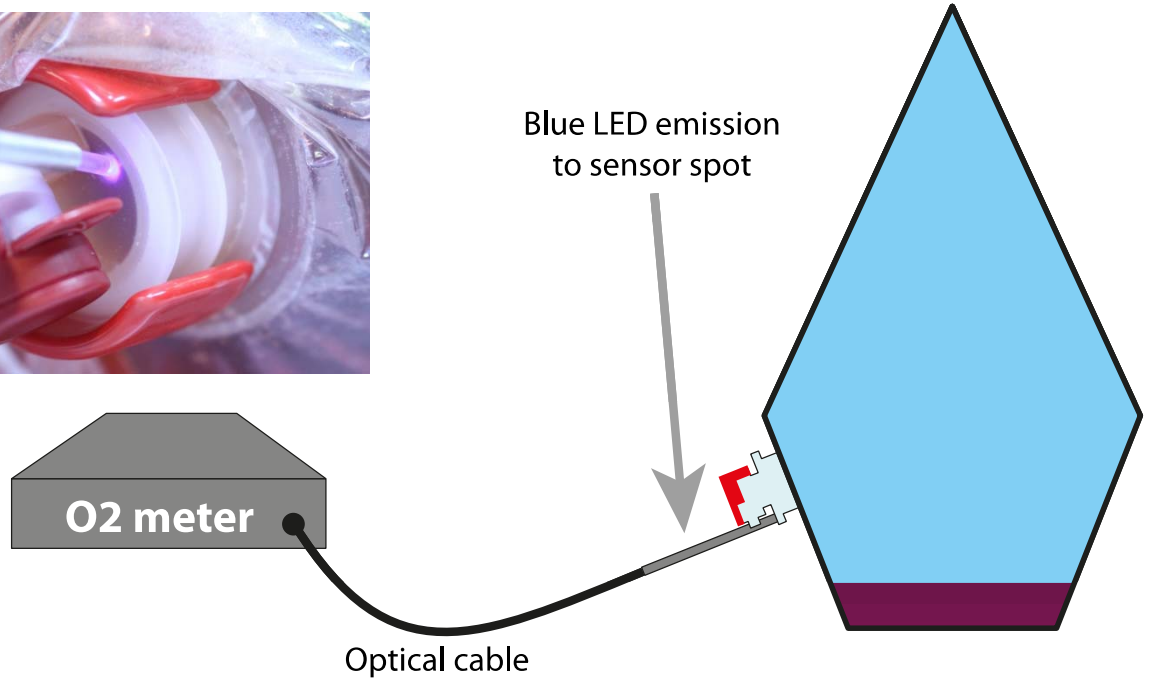


Calculate DO with optodes

Using optical instruments:

- Hold the BIB with the tap below, with the help of a holding clamp in such a way so that only wine (and no air) is filling the tap.
- Make the measurements as soon as possible after the headspace measurements.





Stabilisation time for DO readings with optodes

This stabilisation period for DO (between the beginning of the masurements and when they refect reality) **must still be further studied.**

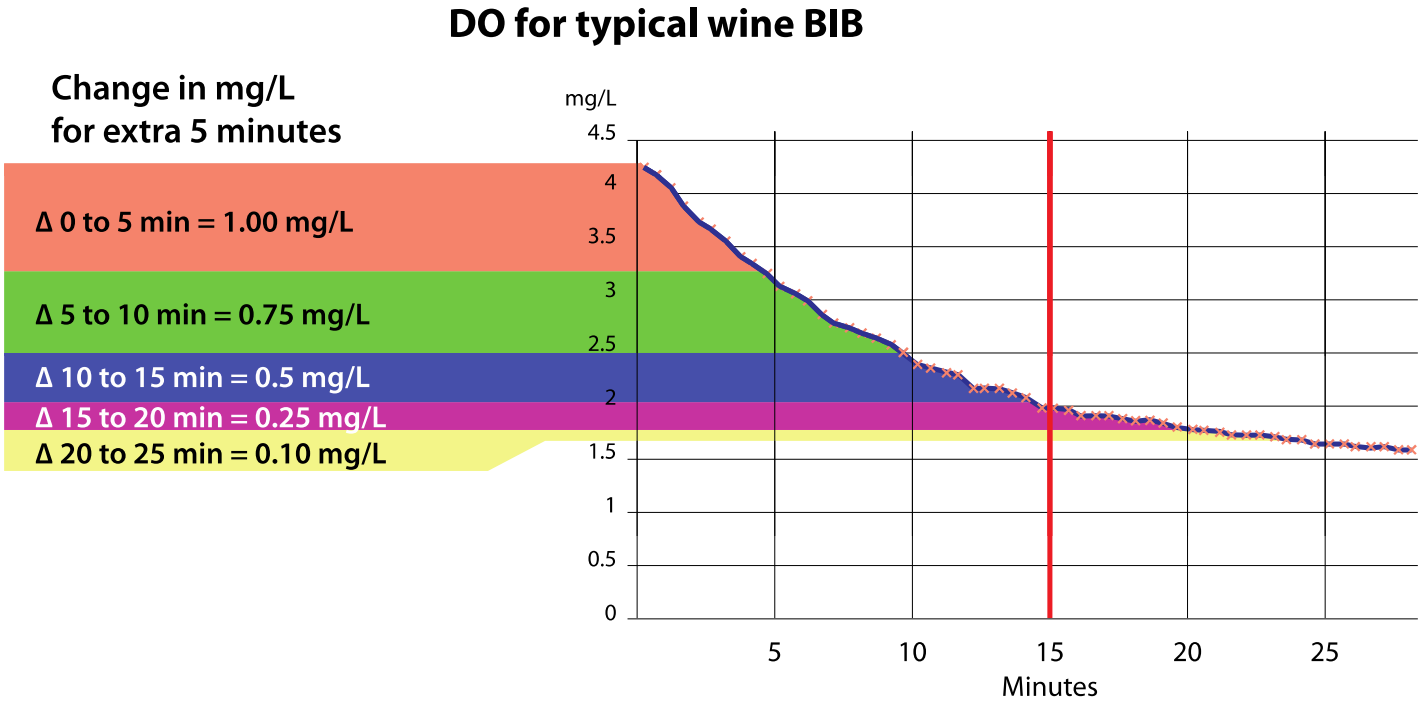
Some sources recommend between 0 and 40 minutes.

This delay must be long enough so as to eliminate the effects of any micro-air bubbles on or around the sensor spot, but the delay must not be so long as to introduce other errors including too much consumption of the oxygen by the wine. In addition, wineries practices generally impose no longer a wait than truly necessary.

At this stage of our research, we recommend a stabilisation time of **15 minutes** for DO readings (non agitated wine) but this recommendation may change as further tests are conducted.

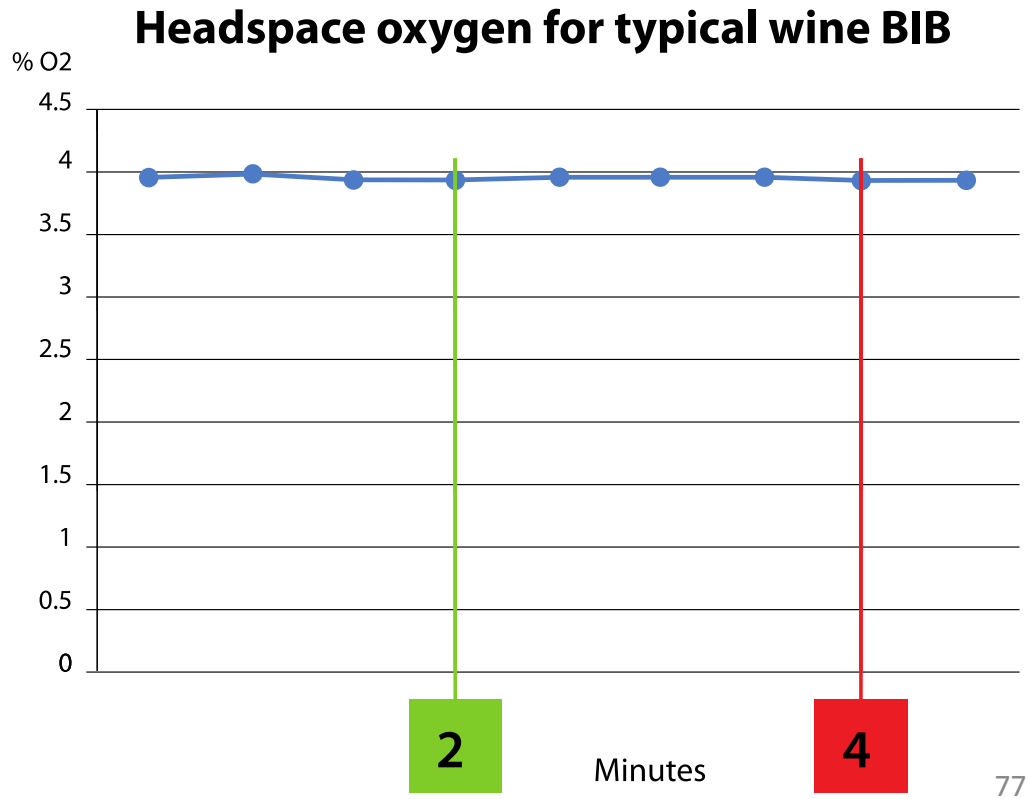
Stabilisation time for DO readings with optodes

Typical DO in unshaked BIBs drops rapidly the first 5 minutes in non-skaken BIB wine and then DO drops more slowly as time goes on. As indicated, our recommended stabilisation time (waiting period) is15 minutes before accepting that the DO value is valid.



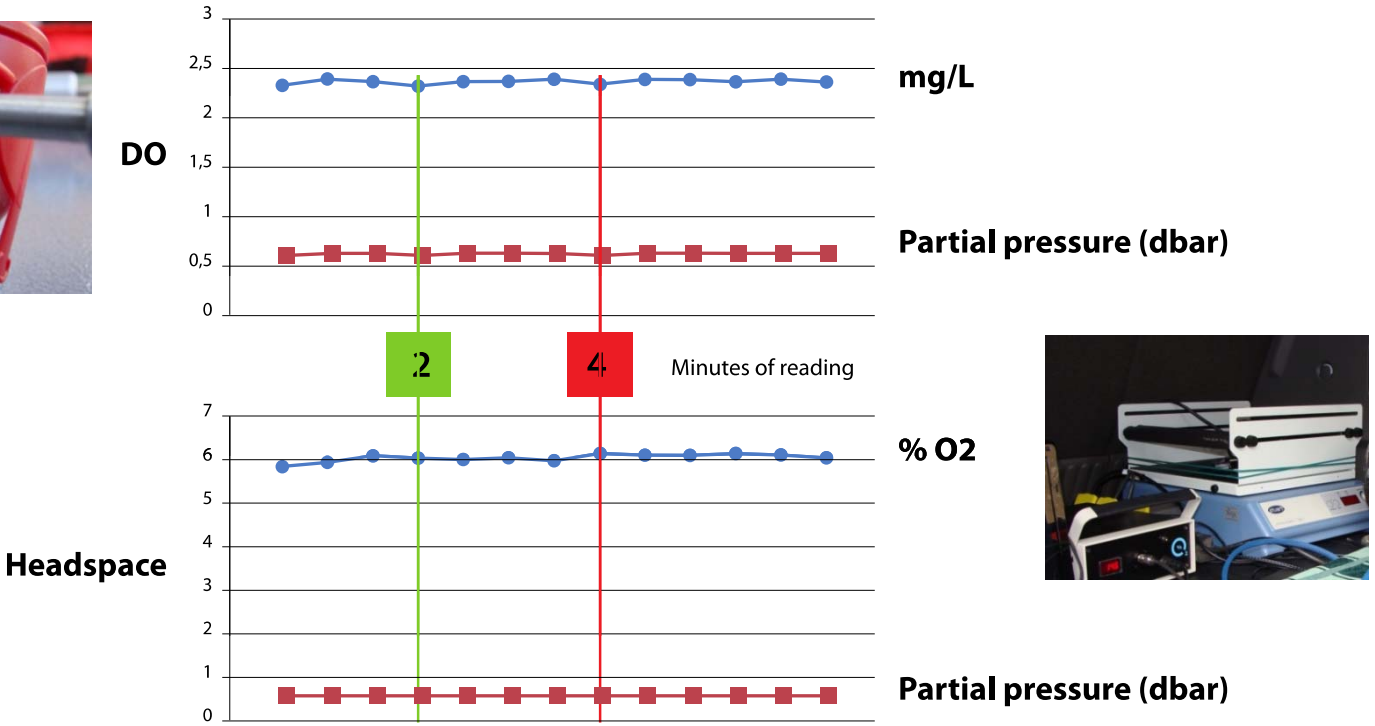
Stabilisation time for Headspace readings with optodes

Typical headspace readings appear to be very stable immediately. The graph below is for the same wine BIB as the previous slide (shown for DO)



Stabilisation time for agitated wine with optodes

After agitation (on an orbital shake table at 275 RPM for 4 minutes), TPO (DO + Headspace) values are very stable immediately. Readings of initial headspace oxygen before agitation should also be taken.



Recommended stabilisation times

The table below summarizes our recommendations:

Type of mesurement	Electrochemical Technologies (electrodes)	Optical technologies (optodes)	
		Without agitation	*With agitation**
Dissolved O_2	Immediate	15 minutes	Immediate
Headspace O_2	Immediate	2 minutes	Immediate

** Agitation with orbital shaker table at 275 RPM for 4 minutes.*

Timing and steps for O_2 measurements with optodes

Times provided below assumes that the instrument is already calibrated, sensor spots are already glued, recommended stabilisation times are applied and the tester is experienced.

The initial DO test (if only one measurement is taken) will take at least 25 minutes and TPO (headspace oxygen and DO) in filled BIBs will take a minimum of another 30 minutes per BIB.

1st step: Measure initial main wine tank DO (stabilisation time 15 minutes + set-up and recording time approx. 10 minutes)

2nd step: Measure headspace oxygen immediately after filling (stabilisation time 2 minutes + set-up and recording time approx. 3 minutes)

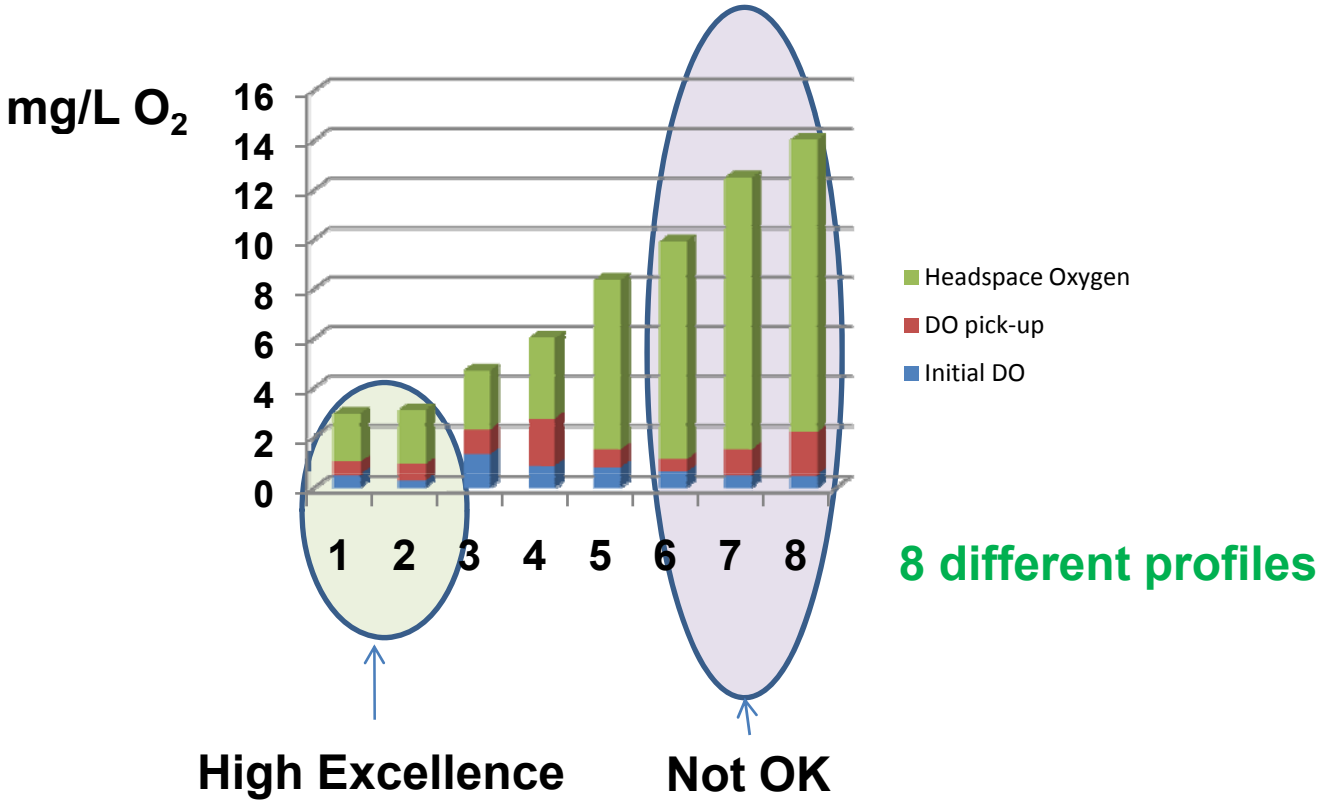
3rd step: Measure headspace volume (set up and measurement time: approx. 5 minutes)

4th step: Measure of filled package DO level (stablisation time: 15 minutes + set-up and recording time approx. 5 minutes)

If an orbital shaker is used, overall measurement time is shortened but results thus obtained may have to be intrepreted differently than results from tests without skaking.

Some TPO Profiles

A comparison of Total Package Oxygen (TPO) in wine BIBs right after filling, observed at various wineries



Wine BIB O_2 measurements / Part 4: Future Research

Part 4: Future research, by Patrick Shea, Vitop

Wine BIB O_2 measurements / Part 4: Future Research

Can we accurately predict wine BIB shelf life?

➡ **Not yet**

BIB Shelf life correlation has been established:

→ **Reasonably well** for: - *SO_2 levels*
- *Microbiological growth*
- *DO pickup during filling*
- *Temperature*

→ **Somewhat** for: - *The type of wine*
- *Package damage*

→ **Very little** for: - *Air cone oxygen*
- *Package OTR*

Shelf-life predictions do not appear to work very well when based upon gas/gas O_2 transmission rates of the barrier film and tap and we know little about the real impact of varying levels of air cone oxygen (volume or % O_2).

Wine BIB O_2 measurements / Part 4: Future Research

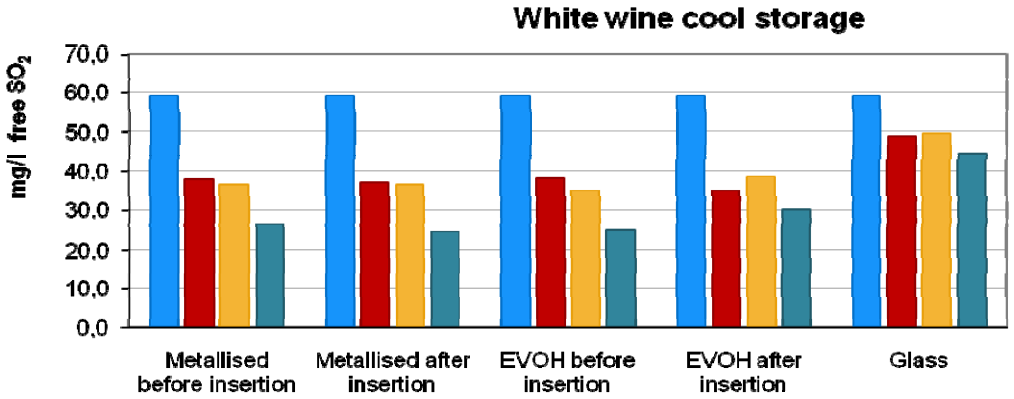
The BIB industry needs to improve its O_2 metrics!

"Dry Test (gas/gas)" OTR results do not reflect real conditions for liquid packaging and often do not appear to be very good indicators of expected shelf-life.

Although some studies do show an overall correlation between "Dry Test (gas/gas)" OTR results and shelf life, we also have:

- The extensive 2004 INRA testing for Performance BIB where a special sealing wax placed over the tap reduced gas/gas OTR by about 42% relative to the unsealed taps. No impact on wine shelf life was observed.

- Several shelf life tests with various films having very different "Dry Test (gas/gas)" OTR results but with little impact on wine BIB shelf life.



Left: comparison between two types of BIB bags (inserted or not in boxes) having different "Dry Test (gas/gas)" OTR results with no difference in shelf life. Presented by C. Schussler (Geisenheim Wine Research Centre) at Performance BIB general meeting in 2008.

Wine BIB O_2 measurements / Part 4: Future Research

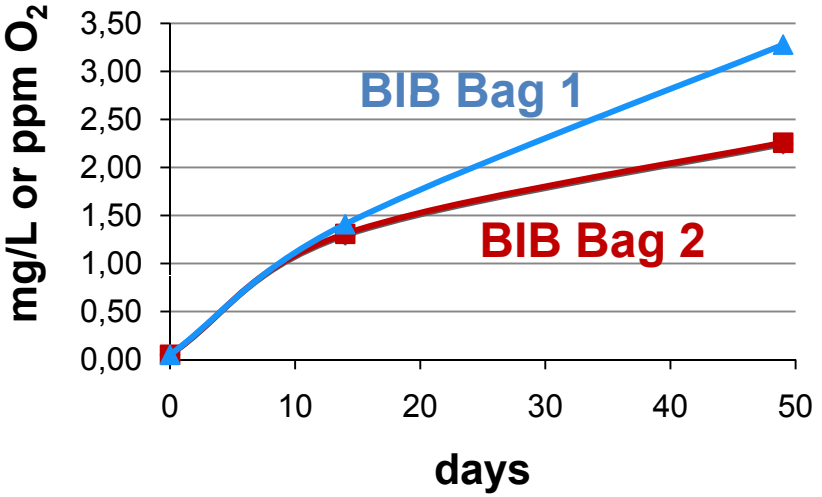
Need for future research

Create model solution (for example, low oxygen, high acid water) in BIB package.

Conduct parallel tests with wine to determine the true correlation between Total Life Cycle Package Oxygen (see schema page 22) in the model solution (in mg/L) and wine BIB shelf-life (and also establishing the degree of correlation with Dry Test OTR results).

Vary key parameters (headspace oxygen % and volume, DO, CO_2 levels, film barrier properties, etc.) in both the model solution and BIBs filled with wine to establish clear correlations between changes in DO levels in the model solution and changes in the wine.

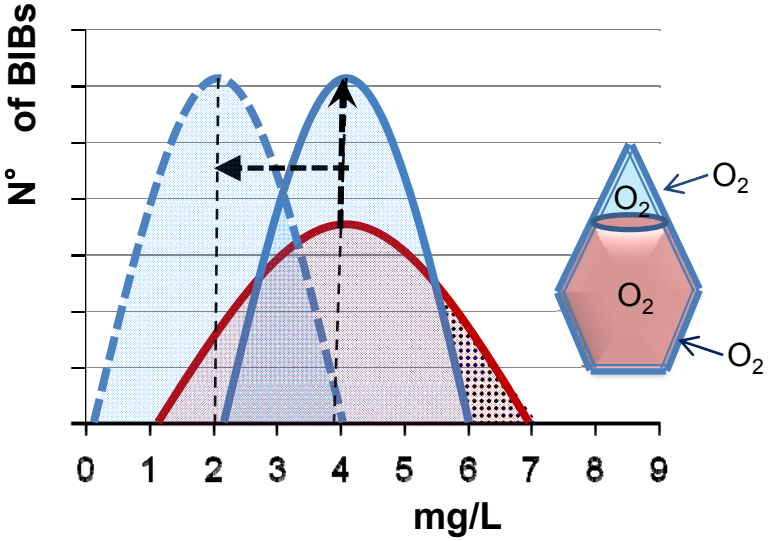
The wine would be evaluated both analytically and sensorial, using also the same wine in a glass bottles as a benchmark. This can build upon the filled package research already pioneered by Georges Crochiere, Aurélie Peychès Bach, Jean-Claude Vidal and others.



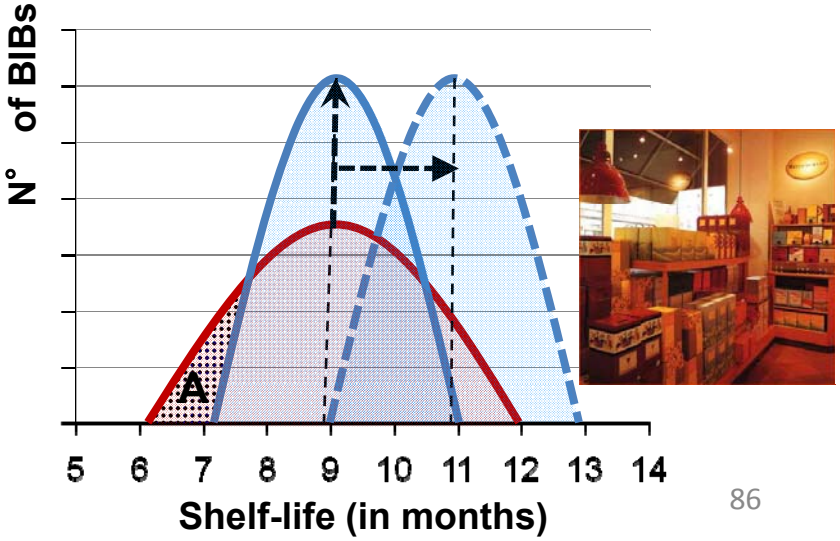
Need for future research

Through better oxygen measurement systems, we can pinpoint further areas of improvement and extend wine BIB shelf-life

Total Life Cycle Package Oxygen goal:
Bell curves tightened (less variance) and/or shifted to the left



Shelf life goal:
Bell curves tightened (less variance) and/or shifted to the right



Wine BIB O_2 measurements / End

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